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MOLECULAR COMPOUNDS AND THEIR SPECTRA. III.

THE INTERACTION OF ELECTRON DONORS AND ACCEPTORS[1]

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ABSTRACT

Extending earlier work,[2] a classification of electron accep-

[2] II of this series: R. S. Mulliken, _J. Am. Chem. Soc._, **74**, 811 (1952).

tors and donors each into a number of types is given in Section II, and illustrative examples of these and of the results of their interaction are tabulated (Tables I-IV). Donors D and acceptors A are here redefined (see Section I) as all those entities during whose interaction transfer of negative charge from D to A takes place, with the formation as end-product either of an additive combination $A_m \cdot D_n$ or of new entities. In all cases of 1:1 interaction, the wave function ψ of A·D (and, formally at least, of the end-products also in the dissociative case) is of the approximate form

$$\psi \approx a\psi_0(DA) + b\psi_1(D^+A^-) , \qquad (1)$$

with appropriate ionic or covalent bonding (or no bonding) between D and A, and between D^+ and A^-, depending on whether A and/or D are closed-shell molecules or ions, or radicals.[3] Donors and acceptors as

Since in ordinary chemistry the free ion H^+ does not occur
(though to be sure it can exist in gas discharges), it appears to be
more realistic to classify it as a <u>virtual</u> than as an actual acceptor
under normal conditions.

II. THE CLASSIFICATION OF DONORS AND ACCEPTORS AND THEIR INTERACTIONS

A general classification of donors and of acceptors each into
several fairly well-marked types is given in Tables I and II, where
each type is characterized in detail. A general scheme displaying the
chief modes of interaction of some of the most important donor-acceptor
pair types is presented in Table III, which is supplemented in Table IV
by a listing of numerous individual examples, together with remarks, in
the case of certain pair-types, about special features of their behav-
ior. The examples include cases of molecular complex formation (D·A),
molecular compound formation (D→A), and bimolecular displacement reac-
tions (A + D ⟶ B + C) between donors D and acceptors A.

Tables I-IV are largely self-explanatory, but a few remarks
on the choice of notation may be worth while. First of all, the sym-
bols have been chosen with considerable care to be as simple and brief
as is consistent with making them reasonably explanatory, convenient
for speaking, writing, or printing, and free from possibilities of con-
fusion with other symbols likely to be used in the same context.

While the broad categories of "donor" and "acceptor" denote
<u>modes of functioning</u>, it is convenient to divide donors and acceptors
each into classes based on their <u>structure</u> before interaction. The
first broad division of donors is into even lone-pair ($\underline{n}$ and $\underline{n}'$), even
bonding-electron (π and σ), and odd-electron (R) radical donors. Simi-
larly, acceptors are classified as even vacant-orbital ($\underline{v}$ and $\underline{v}^*$), even
bonding-electron (π, σ, and σ^*), and odd-electron (Q) radical acceptors.
The individual classes mentioned (there are also others, but these

mentioned are the most important) can conveniently be further divided in some cases into subclasses (for example, the σ acceptor subclass $\underline{h}\sigma$ consists of all neutral-molecule H-acids). The boundaries between classes (or subclasses) are not always sharp, because the structures of actual donors and acceptors are often more or less intermediate between those of two or more classes (see, for example, Table II, Remarks column). It should also be noted that the same molecule, especially if it is a large molecule with various parts, may function under different circumstances sometimes as one kind of a donor, sometimes as another; or again as one or another type of acceptor. For example, even H_2O functions on occasion either as an $\underline{n}$ donor or as an $\underline{h}\sigma_d$ acceptor; and probably sometimes as a σ_d donor, or even perhaps in other ways.

For each of the structure-based classes or subclasses of donors and acceptors, there are at least one, and usually two, characteristic modes of functioning (see Tables I and II). When there are two modes of functioning, one of these is associative, the other is dissociative. These are symbolized by adding subscripts ($\underline{a}$ and $\underline{d}$ respectively) to the class or subclass symbol. The combined symbols are then regarded as denoting subclasses or sub-subclasses. For some classes, only the associative, or else only the dissociative, mode is usual.

For a given donor or acceptor functioning in the dissociative mode (this most often occurs only in the presence of assisting electrostatic or other forces or agencies, for example, those due to an ionizing solvent; see Section VI below), a covalent bond is broken, commonly in a displacement reaction in which ions are formed or exchanged. Actual dissociation of the atoms formerly joined by the broken covalent bond occurs commonly, but not always. For example, it does $\underline{not}$ occur when the π bond of a double bond is broken ($\underline{\sigma\pi}_d$ donors, and $\underline{k\pi}_d$ acceptors), since a σ bond always remains. Even in the case where a σ bond

(single bond) is broken, if two ions are formed, they may still cohere if in the presence of a non-ionizing solvent or in the vapor state (but they are seldom formed under these circumstances), or if in an ionic crystal; commonly, however, they become separated by the process of electrolytic dissociation in an ionizing solvent.

For a donor or acceptor functioning in the associative mode, a covalent bond, either incipient (in loose complexes) or more or less fully developed, and either intoratomic or intermolecular, is formed. Only lone-pair donors and vacant-orbital acceptors are capable of functioning in the associative mode to form strong fairly fully developed new covalent bonds. When bonding-electron (σ and π) donors and acceptors function associatively, it is only with a loosening (partial breaking) of their bonds; if the interaction becomes too strong, it passes over into the dissociative mode (but, as already mentioned, this usually requires the cooperation of additional forces from other molecules).

The class and subclass symbols have been so chosen that they can be simplified, adapted, or extended in various ways according to convenience. For example, one may speak of $\underline{b}\pi$ reagents, or of $\underline{b}\pi$, or simply of π donors; one may speak of $\underline{x}\sigma$ acceptors, or collectively of σ acceptors (including $\underline{x}\sigma$, $\underline{h}\sigma$, $\underline{k}\sigma$, $\underline{l}\sigma$, and perhaps $\underline{h}\sigma^{*}$ and $\underline{k}\sigma^{*}$ acceptors), or collectively of σ_{d} acceptors (including $\underline{x}\sigma_{d}$, $\underline{h}\sigma_{d}$, $\underline{k}\sigma_{d}$, $\underline{l}\sigma_{d}$, and perhaps $\underline{h}\sigma_{d}^{*}$ and $\underline{k}\sigma_{d}^{*}$ acceptors). The notations $\underline{v}^{*}$ and σ^{*} for uni-positive cation acceptors and $\underline{n}'$ for anion acceptors can readily be extended to multiply charged ions (e.g., $\underline{v}^{**}$, $\underline{v}^{***}$, $\underline{n}''$, $\underline{x}\pi^{*}$, etc.). The superscripts * and $'$ have been used, rather than $^{+}$ and $^{-}$, because in some discussions one may wish to refer to donors and acceptors of these types to or from which electrons have been added or subtracted (for example, $\underline{n}'^{+}$ or $\underline{v}^{*-}$).

Finally, it should be pointed out that several changes, believed to bo considerable improvements, have been made in the notation used in provious papers.[2,4] Among other changes, D (for "donor") has been substituted for B (which suggests "base"), and the acceptors formerly called $\underline{d}$ are now $\underline{x}^{\sigma}$, $\underline{h}^{\sigma}$, $\underline{k}^{\sigma}$ (with subscript $\underline{a}$ or $\underline{d}$).

It should be emphasized that the classification scheme as here proposed is still more or less tentative and incomplete. In particular, the classes R and Q and their interactions have been treated only sketchily. It should also be emphasized that the primary purpose of the Tables is not to attempt an authoritative classification of actual molecules and reactions, but rather to give probable or plausible examples to illustrate the functioning of the various donor and acceptor types. Time alone can show just how useful a detailed classification such as that given will be.

TABLE I. ELECTRON

Symbol	Name	Essential Structure[b,c]	Nature
			General Character
n	onium donor	Neutral Even System Containing Relatively Easily Ionized Atomic Lone Pair	Association for Valency Increase
n'	anionic onium donor	Even Ion Q^- or usually Q^-es Containing Easily Ionized Atomic Lone Pair	Same as n
bπ	π donor	Neutral Even System Containing Easily Ionized Bonding π Electrons	$b\pi_a$: Loose Dative Association $b\pi_d$: Strong Dative Association Essentially with Formation of one σ Bond and Loss of one π Bond
bσ	σ donor	Neutral Even System RQ with Rather Weak and Polar R—Q Bond (Polarity R^+Q^-)	$b\sigma_a$: Loose Dative Association (rare) $b\sigma_d$: Ionogenic Displacement Reaction, usually es-assisted
R	radical donor (reducing radical)	System with Relatively Easily Ionized Odd Electron	

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[a] Additional types of donors (e.g., n", bσ') and acceptors could also be described. In general, each type is a mode of functioning, and the same molecule may belong under different circumstances to different types. However, the classification into the major types n and n' (lone-pair electron donors), bπ or bσ (bonding electron donors), and R (odd electron donors) is in terms of the structure of the electronic grouping from which the donated electron comes. On the other hand, the associative and dissociative subtypes (a and d), under each of the bonding electron types, differ with respect to behavior or function.

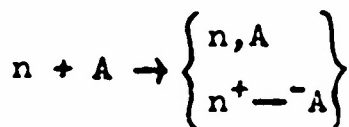DONOR (D) TYPES[a]

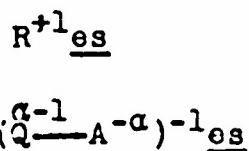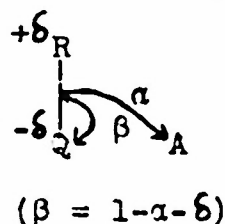| of Donor Action[c]		Examples
VB Description	**MO Description**	
Partial Dative Transfer (cf. Eq. (la)) from lone pair		Amines, alcohols, ethers, ketones, nitriles, CO, sometimes halides, SO_2
$n + A \rightarrow \left\{ \begin{array}{c} n,A \\ n^+ - {}^-A \end{array} \right\}$	$n: + A \rightarrow n: A$	
Same as $\underline{n}$	Same as $\underline{n}$	Es-solvated anions of H-acids, $\underline{e.g.}$, I^-, CH_3COO^-, OH^-, NH_2^-.
$\underline{b\pi}_a$: Partial Dative Transfer from any π bonding pair, with resonance of donor action among all π electrons	$\underline{b\pi}_a$: Partial Dative Transfer from pair occupying most easily ionized bonding π MO	Aromatic (Ar) and Unsaturated (Un) hydrocarbons, and their substitution products with electron-releasing substituents

$\underline{b\sigma}_d$: Partial Dative Transfer from R—Q bonding pair to acceptor with further partial electron transfer R→Q, and liberation of R^+:

$$^{+\delta}R$$
$$_{-\delta}Q \xrightarrow[\beta]{\alpha} A \qquad \xrightarrow{\underline{es}} \qquad R^{+1}\underline{es}$$
$$(Q^{\alpha-1}\text{---}A^{-\alpha})^{-1}\underline{es}$$

$(\beta = 1-\alpha-\delta)$

Alkyl and Aralkyl halides, esters, $\underline{etc.}$, especially if R^+ is resonance-stabilized; solid metals ($\underline{e.g.}$, Na, Mg, Cu).

Univalent metal atoms, H atom, alkyl, aralkyl, and other easily ionized radicals

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[b] "Essential Structure" refers of course, in complicated cases, only to the region where the donor or acceptor action takes place.

[c] The symbol $\underline{es}$ denotes the presence of a source of electrostatic forces which stabilizes the system in question: usually an attached polar solvent molecule or molecules, or sometimes a companion ion or ions, as in ion-pairs, ion-clusters, or solid salt.

TABLE II. ELECTRON

Symbol	Name	Essential Structure	Nature
			General Character
$\underline{v}$	vacant-orbital acceptor	Neutral Even System in which an Orbital or Orbitals of Relatively High $\underline{E}$ (Electron Affinity) are vacant	Association for Valency Increase
$\underline{v}^{*}$	cationic vacant-orbital acceptor	Even Ion R^{+} or Usually R^{+}es with High-E Localized Orbital Vacant	Same as $\underline{v}$
$h\sigma_{d}^{*}$ and $k\sigma_{d}^{*}$	cationic dissociative σ acceptor	Even cation of structure DH^{+}es (type $h\sigma^{*}$), DR^{+}es (type $k\sigma^{*}$), or in general $(D\rightarrow)_{n}R^{n+}$es (generalized $k\sigma^{*}_{m}$ type).	Always Dissociative (σ_{d}^{*}). Displacement reaction: acceptance of stronger base in place of weaker

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$\underline{a}$ See notes $\underline{a}$, $\underline{b}$, and $\underline{c}$ of Table I.
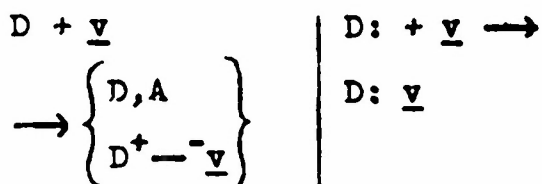
$\underline{b}$ There appear to be two main driving forces behind acceptor action:
(1) the tendency of atoms with vacant orbitals to pick up electrons
to form additional bonds (valency increase); (2) the tendency of
electronegative atoms in a molecule to become negatively charged

ACCEPTOR (A) TYPES[a]

of Acceptor Action[b]		Examples	Remarks
VB Description	MO Description		
Partial Dative Acceptance (cf. Eq. (1a)) Into Vacant Orbital:		BMe_3, $AlMe_3$, BX_3, AlX_3, FeX_3, $ZnCl_2$, $HgCl_2$, O atom, $SnCl_4$(?), SiF_4(?)	See Remarks A1 and A2 (following this Table)
$D + \underline{v}$ $\rightarrow \begin{Bmatrix} D,A \\ D^+\!-\!^-\underline{v} \end{Bmatrix}$	$D: + \underline{v} \longrightarrow$ $D: \underline{v}$		
Same as $\underline{v}$	Same as $\underline{v}$	$Ag^+\underline{es}$, $NO_2^+\underline{es}$, $HSO_3^+\underline{es}$, Carbonium cations Ak^+ or $Ak^+\underline{es}$	See Remarks B1, B2, B3, and B4 (following this Table)
In general: $p\overline{D} + (D\rightarrow)_m R^{n+}\underline{es} \longrightarrow$ $(D\rightarrow)_q(\overline{D}\rightarrow)_p R^{n+}\underline{es} + pD$ In particular, if acceptor is $DR^+\underline{es}$ or $DH^+\underline{es}$,		$\begin{cases} \underline{h}\sigma_d^{*}: H_3O^+\underline{es}, NH_4^+\underline{es} \\ \underline{k}\sigma_d^{*}: Ag(NH_3)_2^+\underline{es}. \\ Ag^+\underline{aq} \text{ may belong here, but is more conveniently regarded as } \underline{v}^*. \end{cases}$	See Remarks B1, B2, B3, and B4 (following this Table)
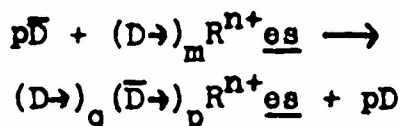
$\begin{array}{l} ^{-\delta}D^+\underline{es} \quad\quad D \\ \quad\downarrow\!\!\overset{\alpha}{\quad} \\ ^{+\delta}R \xleftarrow{\beta} \overline{D} \quad (R\!-\!\overline{D})^+\underline{es} \end{array}$
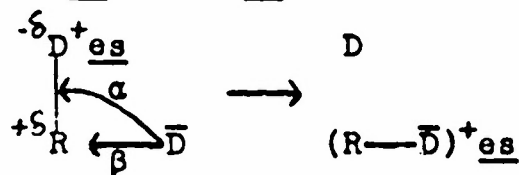
Here D^+ and D play the same roles as Q and Q^- in σ_d acceptor action.
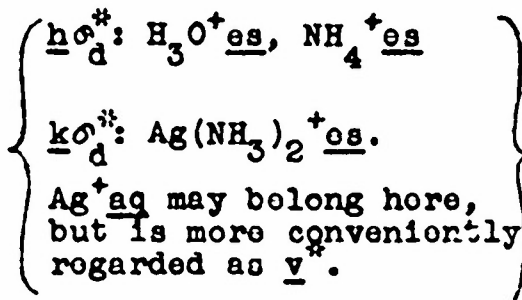
(electronegativity satisfaction). The first of these is largely confined to $\underline{v}$ acceptors, while the second is present for most acceptors. In π-electron systems resonance effects are also important. In all types of acceptors, acceptor strength increases on increased loading with electronegative atoms.

TABLE II. ELECTRON ACCEPTOR

(Symbol)	(Name)	(Essential Structure)	(Nature
			(General Character
$\underline{x}\pi$	π acceptor	Neutral Even System Containing Bonding π Electrons Relatively Strongly Held	$\underline{x}\pi_a$ or $\underline{k}\pi_a$: Loose Dative Association
$\underline{k}\pi$	ketoid π acceptor	Neutral Even System Usually of Structure Z=O (or Resonating Z=O) Containing Strongly Polar π bond(s)	$\underline{x}\pi_d$ or $\underline{k}\pi_d$: Association (for Better Saturation and Electronegativity Satisfaction) with Formation of one σ and Breaking of one π Bond

(A) TYPES[a] (CONTINUED)

of Acceptor Action[b])		(Examples)	(Remarks)
VB Description	MO Description)		

$x\pi_a$ or $k\pi_a$: Partial Acceptance of π electron by any π bonding pair, converting the latter partially into an odd π electron (which gives dative bonding to donor) plus π lone pair; with resonance of this action among all π electrons.
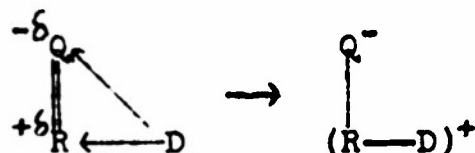
$x\pi_a$ or $k\pi_a$: Partial Acceptance of electron into lowest-energy (highest-E) antibonding π MO, with dative bonding to donor.

$x\pi$: Aromatic or Unsaturated Hydrocarbons with electronegative or electrophilic substituents. For example, trinitrobenzene, maleic anhydride.

$k\pi_d$: Partial Electron Acceptance by both R and Q with loss of R—Q π bond and formation of R—D bond:

usually followed by rearrangements or further reaction.

$k\pi$: RHCO, RR'CO, RCN, CO_2, SO_2 ($O \overset{S}{\searrow} O$), SO_3 ($\overset{O}{\underset{O}{\swarrow}} S \rightarrow O$).

See Remark C (following this Table)

on "Quantum-Mechanical Methods in Valence Theory". This Report is obtainable from L. M. McKenzie, Head, Physics Branch, Office of Naval Research, Department of Navy, Washington 25, D.C.

here defined correspond closely to nucleophilic and electrophilic reagents as defined by Ingold or, except for the inclusion here of donor and acceptor radicals, correspond rather well to bases and acids as defined by G. N. Lewis. In Section III, the applicability of an extension of Eq. (1) to crystalline molecular compounds is considered briefly.[3]

A brief discussion and listing of possible or probable known charge-transfer spectra [2,4] of donor-acceptor molecular complexes are given in Section IV and Table IV. Sections V-VIII contain further elucidation of matters discussed in Sections I-II and in Ref. 2.

[4] I of this series: R. S. Mulliken, J. Am. Chem. Soc., 72, 600 (1950).

The energy U of interaction between a donor and acceptor as a function of a charge-transfer coordinate C (a kind of reaction coordinate, so defined as to increase from 0 to 1 with increasing transfer of electronic charge from D to A) is studied in Section IX for interactions between donor-acceptor pairs of the various classes defined here. In many cases, there should be two important minima in the $U(C)$ curve, namely one for a loose "outer complex" for small C, and one for a tighter "inner complex", of either dative or ion-pair character, for large C (see Figs. 1-2). In any particular case, one of these is the stable form, while the other is an excited or activated state (lower in energy, however, than the activation barrier which usually intervenes between them). However, in many cases where the donor and acceptor form only a loose outer complex or none at all in the vapor state or in an inert solvent, the inner complex, if of ionic type, may become the

TABLE II. ELECTRON ACCEPTOR

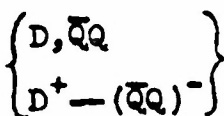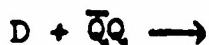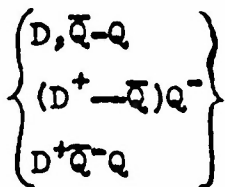| (Symbol)	(Name)	(Essential Structure)	(Nature (General Character
$\underline{x}\sigma$	halogenoid σ acceptor	Neutral Even System Q_2 or $\bar{Q}Q$, with Usually Weak σ Bond between Electro-negative Atoms or Radi-cals	$\underline{x}\sigma_a$ (also, rarely, $\underline{h}\sigma_a$): Loose Dative Association for Better Electro-negativity Satis-faction.
$\underline{h}\sigma$ and $\underline{k}\sigma$	dissociative σ acceptors	Neutral Even System HQ or RQ with Usually Rela-tively Strong σ Bond	$\underline{x}\sigma_d$, $\underline{h}\sigma_d$, or $\underline{k}\sigma_d$: Dissociation, usually es-as-sisted, to Form Q^-es.
$\underline{h}\sigma^\#$ and $\underline{k}\sigma^\#$ (see above)			
Q	radical acceptor (oxidizing or electrophilic radical)	Odd-Electron System with Relatively High Electron Affinity	

(A) TYPES[a] (CONTINUED)

| of Acceptor Action[b])		(Examples)	(Remarks)
VB Description	MO Description)		
$x\sigma_a$: $D + \bar{Q}Q \longrightarrow$ $\begin{cases} D, \bar{Q}-Q \\ (D^+ - \bar{Q})Q^- \\ D^+\bar{Q}^-Q \end{cases}$	$D + \bar{Q}Q \longrightarrow$ $\begin{cases} D, \bar{Q}Q \\ D^+ - (\bar{Q}Q)^- \end{cases}$ Accepted electron in $(\bar{Q}Q)^-$ goes into strongly anti-bonding σ MO, which weakens on dissociation.	$x\sigma$: Halogen molecules X_2 and XY, $Ph_3CH(?)$	See Remark D (following this Table)
$\underline{h}\sigma_d$ or $\underline{k}\sigma_d$:	$D + RQ \longrightarrow$ $\begin{cases} D, RQ \\ D^+ - RQ^- \end{cases} \rightarrow (Q^- out)$ Accepted electron in RQ^- goes into strongly antibonding σ MO which weakens on dissociation.	$\underline{h}\sigma$: All neutral H-acids, including HX, Water, Alcohols. $\underline{k}\sigma$: Organic Halides, Esters.	See Remarks E1, E2, and E3 (following this Table)
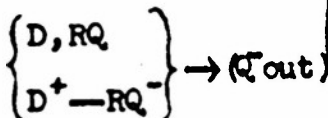
Partial Electron Acceptance by Q from both D and R (or H) with liberation of Q^- and formation of D—R bond.

$Q^- \underline{es}$

$\xrightarrow{\underline{es}}$

$(R^{1-\alpha} - D^\alpha)^{+1}\underline{es}$
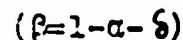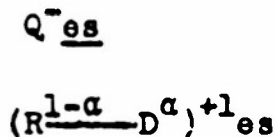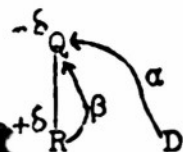
$(\beta = 1 - \alpha - \delta)$
(See Eq. (5) for example with further details)

Halogen atoms,
H atom, NO_2, acid
radicals

TABLE II. ELECTRON ACCEPTOR (A) TYPES[a] (CONTINUED)

REMARKS

A1: These and $\underline{v}^{\#}$ are <u>the</u> typical Lewis acids.

A2: Really the vacant orbital is not quite vacant, because of resonance structures like $\overset{X}{\underset{X}{\diagdown}} B^- = X^+$ or $Cl^+ = Hg^= = Cl^+$, and to this extent $\underline{v}$ acceptors are $\underline{k\pi}$ acceptors like $RR'C=O$ and $O=C=O$.

B1: The $\underline{v}^{\#}$ acceptors are typical Lewis acids. Luder calls the $\sigma^{\#}$ acceptors secondary Lewis acids.

B2: Ions of structure $R^+\underline{sl}$ are classified as $\underline{v}^{\#}$ or as $\underline{k\sigma}^{\#}$ according as the solvent molecules ($\underline{sl}$) are held primarily by $\underline{es}$ or by donor action and so regarded as accessory or as constitutive. In doubtful cases, the $\underline{v}^{\#}$ classification is the more convenient. Ions of structure $H^+\underline{sl}$ are almost always most properly $\underline{h\sigma}^{\#}$ rather than $\underline{v}^{\#}$.

B3: However, even definitely $\underline{k\sigma}^{\#}$ or $\underline{h\sigma}^{\#}$ acceptors are often conveniently regarded <u>by courtesy</u> as $\underline{v}^{\#}$, by ignoring $\underline{sl}$ in $R^+\underline{sl}$ or $H^+\underline{sl}$; for example, $H_3O^+\underline{aq}$ may be regarded as H^+.

B4: The type $\underline{h\sigma}^{\#}$ comprises precisely the conjugate acids DH^+ of all bases D. Examples include among others ArH^+ and UnH^+. However, $UnH^+ \equiv R^+$ ($\underline{e.g.}$, $Un = C_2H_4$) functions more often associatively as a $\underline{v}^{\#}$ acceptor in its own right than dissociatively as an $\underline{h\sigma}_d^{\#}$ acceptor.

C: $\underline{k\pi}$: The $\underline{k\pi}$ and $\underline{v}$ acceptors are not separated by any sharp boundary, but a continuous range of intermediate cases is possible.(See Remarks on $\underline{v}$ acceptors.)

D: $\underline{x\sigma}$: In X_2 or VX, weak σ bonds, $E^{vert} > 0$, small but increasing strongly, during dissociation to limiting Value E_X.

E1: The $\underline{h\sigma}$ class consists precisely of all the neutral H-acids.

E2: In HX or RX, strong polar σ bonds, $E^{vert} \ll 0$ but becomes > 0 during dissociation, with limiting Value E_X.

TABLE II. ELECTRON ACCEPTOR (A) TYPES[a] (CONTINUED)

REMARKS (continued)

<u>E3</u>: HQ and RQ are sometimes described as secondary Lewis acids, con-
ceived as formed from the primary Lewis acid H^+ or R^+ and the
base Q^-.

TABLE III. SOME DONOR-

Acceptor Type \ Donor Type	$\underline{n}$	$\underline{n}'$ ⟨usually $Q^-\underline{es}$⟩
$\underline{v}$	DATIVE	(Sy) DATIVE
$\underline{v}^{\#}$ ⟨usually $R^+\underline{es}$⟩	(Sy) DATIVE	DATIVE forming RQ or Sy DATIVE
π $\underline{x}\pi$ $\begin{cases}\underline{x}\pi_a\\\underline{x}\pi_d\end{cases}$	dative	Q—$x\pi$ σ bond formed datively, with loss of one π bond
$\underline{k}\pi$ ⟨usually Z=O⟩ $\begin{cases}\underline{k}\pi_a\\\underline{k}\pi_d\end{cases}$	DATIVE $(\underline{es})$: $\underline{n}^+$—Z—O^- $\longrightarrow$	$\underline{es}$-dative Q—Z—$O^-\underline{es}$ $(\longrightarrow)$
σ $\underline{x}\sigma$ ⟨QQ⟩ $\begin{cases}\underline{x}\sigma_a\\\underline{x}\sigma_d\end{cases}$	dative $(\overset{es}{\longrightarrow})$ $\begin{cases}\underline{es}: [\underline{n}\overline{Q}]^+Q^-\underline{es} \;(\longrightarrow)\\ \underline{es},\underline{v}: [\underline{n}\overline{Q}]^+[\underline{v}Q]^-\underline{es}(\longrightarrow)\end{cases}$	Sy DATIVE
$\underline{h}\sigma$ ⟨HQ⟩ $\begin{cases}\underline{h}\sigma_a\\\underline{h}\sigma_d\end{cases}$	(see Table IV) $\underline{es}: [\underline{n}H]^+Q^-\underline{es}$	Sy DATIVE $Q_DH + Q^-_A\underline{es}$
$\underline{k}\sigma$ ⟨RQ⟩ $\begin{cases}\underline{k}\sigma_a\\\underline{k}\sigma_d\end{cases}$	(see Table IV) $\underline{es}: [\underline{n}R]^+Q^-\underline{es}$	$Q_DR + Q^-_A\underline{es}$
$\underline{1}\sigma_d$ ⟨$\underline{n}\underline{v}$⟩	$\underline{n}\underline{v} + \overline{\underline{n}}$	
σ^* $\underline{x}\sigma_d^{\#}$ ⟨$[\overline{Q}D]^+\underline{es}$⟩		
$\underline{h}\sigma_d^{\#}$ ⟨$[HD]^+\underline{es}$⟩	$[\underline{n}H]^+\underline{es} + D$	QH + D
$\underline{k}\sigma_d^{\#}$ ⟨$[RD]^+\underline{es}$⟩	$[\underline{n}R]^+\underline{es} + D$	QR + D
$Q\{Q_v, Q_\pi, Q_\sigma\}$		

ACCEPTOR REACTION-TYPES

$\underline{b\pi}$		$\underline{b\sigma}$ (commonly RQ)		R
$\underline{b\pi}_a$	$\underline{b\pi}_d$	$\underline{b\sigma}_a$	$\underline{b\sigma}_d$	$\{R_n, R_\pi, R_{,\,}\}$
dative			$\underline{es}:R^+[Q\underline{v}]^-\underline{es}$	
dative	$b\pi$—R σ bond formed dat-ively, with loss of one π bond		$R_D^+\underline{es} + QR_A$	
dative				
dative				
dative		dative		
	$\begin{cases}\underline{es}: [\pi\overline{Q}]^+Q^-\underline{es}\ (\longrightarrow) \\ \underline{es},\underline{v}: [\pi\overline{Q}]^+[\underline{v}Q]^-\underline{es}(\longrightarrow)\end{cases}$			
(see Table IV)	$\begin{cases}\underline{es}: [\pi H]^+Q^-\underline{es} \\ \underline{es},\underline{v}: [\pi H]^+[\underline{v}Q]^-\underline{es}\end{cases}$		$(Q_DHQ_A)^- + R^+$ perhaps $\underline{es}$: $Q_DH + R^+Q_A\underline{es}$	$R^+Q^- + H$
(see Table IV)				$R_D^+Q^- + R_A$
			$\begin{cases}\text{perhaps} \\ QH + R^+\underline{es} + D\end{cases}$	
dative				RQ or R^+Q^-

TABLE III. SOME DONOR-ACCEPTOR REACTION-TYPES (<u>CONTINUED</u>)

EXPLANATION OF TABLE

For detailed descriptions of donor (D) and acceptor (A) types and notation, see Tables I and II. Subscripts <u>a</u> and <u>d</u> appended to donor and acceptor symbols of the σ and π classes indicate <u>associative</u> (<u>a</u>) or <u>dissociative</u> (<u>d</u>) functioning. For any donor-type acceptor-type pair, Table III describes the reaction-type by stating briefly the nature of the <u>initial</u> <u>reaction-product</u> or products for a direct bimolecular reaction between donor and acceptor. The word "dative" indicates a <u>loose</u> dative complex, the word "DATIVE" a dative complex or compound which in typical examples is strongly bound. For specific examples of the reaction-types indicated in Table III, see Table IV.

In Table III, certain symbols and punctuation marks are used only with definite explicit meanings, as follows: $\langle ... \rangle$ is used only with a brief structural description of a donor or acceptor type; $(...)$ means that the indicated behavior <u>may</u> or <u>may not</u> occur in a given example depending on circumstances, and/or that it occurs in some examples but not in all; $\longrightarrow$ means that an indicated reaction product is an unstable or stable intermediate which normally reacts further (either intramolecularly and/or, usually, with other molecules). <u>Subscripts</u> D and A serve, when necessary, to identify different R and/or Q radicals in the reaction-products in terms of their origin in the donor or acceptor reactant. The <u>colon</u> following <u>es</u> or <u>es,v</u> indicates that the reaction occurs <u>conditionally</u> (in most cases, <u>only</u> conditionally), through cooperative action of agents acting electrostatically (<u>es</u>), or through the cooperation of an auxiliary <u>v</u> acceptor plus <u>es</u> agents (<u>es,v</u>). The symbol <u>Sy</u>, standing for <u>symmetrization</u>, denotes a process in which, when an incoming donor or acceptor joins a partner containing identical (or sufficiently similar) atoms, all the like atoms become <u>mutually</u> equival-

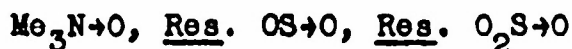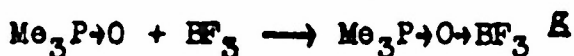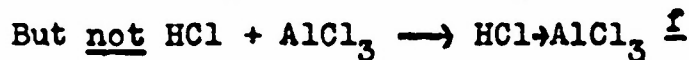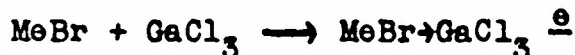TABLE III. SOME DONOR-ACCEPTOR REACTION-TYPES (CONTINUED)

ent (or nearly so) in position and internal electronic distribution.

Tables III and IV are not exhaustive: (a) additional D and A types exist, e.g., $\underline{n}''$ and σ' donors, $\underline{v}^{**}$, $\underline{v}^{***}$, and π^{*} acceptors, etc; (b) additional reaction-types corresponding to some of the blanks in Table III exist, but only those types are listed in Table III of which examples are given in Table IV; (c) reaction-types involving R donors and Q acceptors are indicated only very sketchily. Tables III and IV are not intended to imply that the actual reaction mechanism for a given donor and acceptor is necessarily always (or perhaps ever) the direct bimolecular mechanism indicated in the tables. However, the reaction-types listed are believed to be correct at least as to over-all driving force and over-all result, although whether for any given individual ex-ample they go at all, or reach an equilibrium, or go to completion, de-pends of course on the acceptor and donor strengths of the particular reactants. The reaction-types listed are believed also to correspond in most cases to reaction mechanisms which are likely to be realized in practice at least under some circumstances. As is well known, over-all bimolecular reactions often proceed actually in steps, with the monomo-lecular or quasi-monomolecular ionization process $RQ \longrightarrow R^{+}\underline{sl} + Q^{-}\underline{sl}$ as an initial step, the solvent ($\underline{sl}$) action involved being sometimes purely electrostatic ($\underline{es}$) and sometimes partly or wholly a donor or acceptor action. The $\underline{v}^{*}$ or σ_{d}^{*} acceptor $R^{+}\underline{sl}$ and/or the $\underline{n}'$ or σ_{d}' donor (σ_{d}' is of structure $\underline{n}'\underline{v}$) then react further. (The ionization process is the rever-sal of a donor-acceptor reaction of type $\underline{v}^{*}$ or σ_{d}^{*} plus $\underline{n}'$ or σ_{d}' $\longrightarrow RQ$.) In a few examples in Tables III and IV, processes involving the assist-ance of an auxiliary acceptor or donor (usually a $\underline{v}$ acceptor) have been indicated. No opinion is implied here as to whether ever, or how often, the actual reaction mechanism in such processes is termolecular.
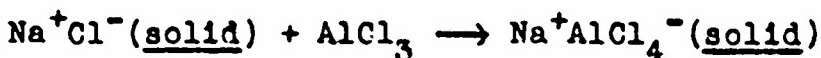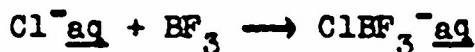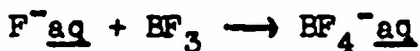
TABLE IV.

SOME EXAMPLES OF DONOR-ACCEPTOR COMPLEXES (D·A), COMPOUNDS (D→A), AND
PROBABLE REACTIONS (D + A ⟶ PRODUCTS), AND APPROXIMATE WAVELENGTHS λ
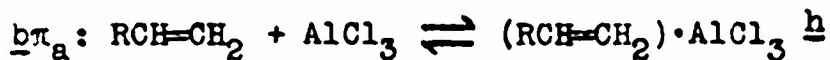OF SOME PROBABLE CHARGE-TRANSFER ABSORPTION SPECTRA PEAKS[a,b,c]
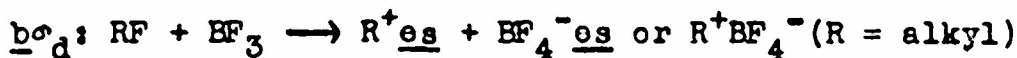
1. Type n + v [d]

$Et_2O + BF_3 \longrightarrow Et_2O{\to}BF_3$

$Me_3N + BMe_3 \longrightarrow Me_3N{\to}BMe_3$

$Me_3N + AlCl_3 \longrightarrow Me_3N{\to}AlCl_3$

$MeCN + BF_3 \longrightarrow MeCN{\to}BF_3$

$MeBr + GaCl_3 \longrightarrow MeBr{\to}GaCl_3$ [e]

But not $HCl + AlCl_3 \longrightarrow HCl{\to}AlCl_3$ [f]

$Me_3P{\to}O + BF_3 \longrightarrow Me_3P{\to}O{\to}BF_3$ [g]

$Me_3N{\to}O$, Res. $OS{\to}O$, Res. $O_2S{\to}O$

2. Type n' + v (usually Q⁻es + v)

$F^-\underline{aq} + BF_3 \longrightarrow BF_4^-\underline{aq}$

$Cl^-\underline{aq} + BF_3 \longrightarrow ClBF_3^-\underline{aq}$

$Na^+Cl^-(\underline{solid}) + AlCl_3 \longrightarrow Na^+AlCl_4^-(\underline{solid})$

3. Type bπ + v

$b\pi_a$: $RCH{=}CH_2 + AlCl_3 \rightleftharpoons (RCH{=}CH_2){\cdot}AlCl_3$ [h]

4. Type bσ + v

$b\sigma_d$: $RF + BF_3 \longrightarrow R^+\underline{es} + BF_4^-\underline{es}$ or $R^+BF_4^-$ (R = alkyl)

(in RF as es solvent, or in aliphatic hydrocarbon solvent)

$NOCl + AlCl_3 \longrightarrow NO^+AlCl_4^-(\underline{solid})$

$COCl_2 + AlCl_3 \longrightarrow COCl^+\underline{sl} + AlCl_4^-\underline{sl}$
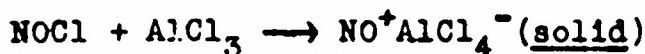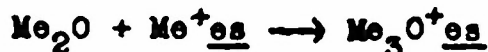
(in suitable solvent; in liquid $COCl_2$, mechanism may be
through ionization of $COCl_2$)

TABLE IV (CONTINUED)

5. Type n + v#

CH_2I_2 + Ag^+aq $\rightleftharpoons$ $CH_2I_2 \cdot Ag^+$aq $\underline{l}$
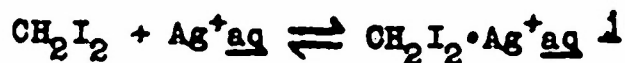
  (here perhaps Ag^+aq is more nearly of $\underline{k\sigma}_d^\#$ than $\underline{v}^\#$ type)

Me_2O + Me^+es $\longrightarrow$ Me_3O^+es

  (in MeF solution, after MeF + BF_3 $\longrightarrow$ Me^+es + BF_4^-es)

$2NH_3$ + $Ag^+NO_3^-$(crystal) $\xrightarrow{es}$ $(H_3N\rightarrow)_2Ag^+$es + NO_3^-es

  (in aq or aqueous ammonia, with aq as es)

6. Type n' + v# $\underline{d}$

Cl^-sl + Ph_3C^+sl $\rightleftharpoons$ Ph_3CCl $\underline{k}$
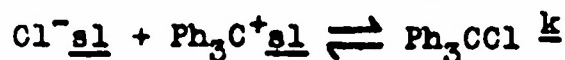
  in liquid SO_2, nitromethane, or acetone (sl action in Cl^-sl

  partly dative: see under n' + kx (Part 10 of this Table))
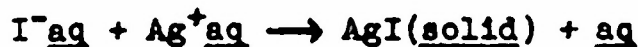
I^-aq + Ag^+aq $\longrightarrow$ AgI(solid) + aq

  (see remarks on Ag^+aq under n + $\underline{v}^\#$ (Part 5 of this Table))

$2CN^-$aq + Ag^+aq $\longrightarrow$ $[Ag(CN)_2]^-$aq

7. Type bx + v#

bπ$_a$: Bz + $Ag^+ClO_4^-$ $\rightleftharpoons$ $Bz \cdot Ag^+ClO_4^-$, and $(Bz \cdot Ag^+ \cdot Bz)ClO_4^-$?

  (in benzene solution)

MePh + Ag^+aq $\rightleftharpoons$ $MePh \cdot Ag^+$aq ($\lambda 2300$?) $\underline{m}$

  and $aqAg^+ \cdot MePh \cdot Ag^+$aq
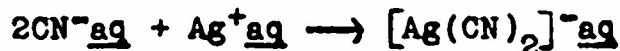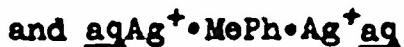
  (in aqueous solution; here see remarks on Ag^+aq under n + $\underline{v}^\#$

  (Part 5 of this Table))

bx$_d$: Bz + NO_2^+es + HSO_4^-es $\longrightarrow$ $[BzNO_2]^+$es + HSO_4^-es $\longrightarrow$ $PhNO_2$ + H_2SO_4

  (in sulfuric acid solution, with sulfuric acid as es)

Bz + R^+es + $AlCl_4^-$es $\longrightarrow$ $[BzR]^+$es + $AlCl_4^-$es $\longrightarrow$ PhR + HCl + $AlCl_3$
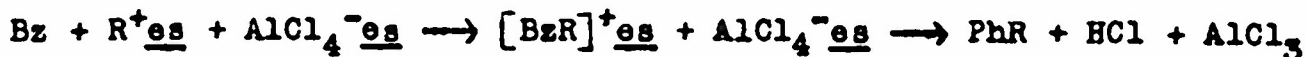
  (e.g., perhaps EtCl solution of $AlCl_3$ ($\longrightarrow$ Et^+es + $AlCl_4^-$es) + Bz)

stable form under the cooperative action of a suitable active solvent. The latter functions by solvation of the inner complex or its ions, acting either mainly electrostatically, or in some cases mainly as an auxiliary donor or acceptor (double-complex formation). The formation of ion-pair clusters or ionic crystals (e.g., $NH_3 + HCl \longrightarrow NH_4^+Cl^-$) can play the same role as that of an electrostatically functioning solvent in stabilizing the inner complex of a donor-acceptor pair. In a few interaction types, a "middle complex" is important (cf. Fig. 3), corresponding either to an activated complex or intermediate in a reaction such as those involving a Walder inversion, or to a stable association product. Section X contains improvements and errata for the previous papers of this series.

I. THE INTERACTION OF DONORS AND ACCEPTORS

In chemical theory, the usefulness of G. N. Lewis's broad conception[5,6] of what should be meant by the words acid and base has

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[5] G. N. Lewis, Valence and The Structure of Atoms and Molecules (The Chemical Catalog Company: New York, 1923), see especially pp. 142, 133, 113, 107; J. Franklin Institute, 226, 293 (1938).

[6] W. F. Luder and S. Zuffanti, The Electronic Theory of Acids and Bases (John Wiley and Sons: New York, 1946).

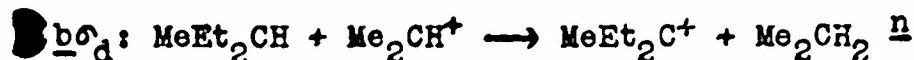become increasingly evident. However, since these words (especially acid) are commonly used with narrower meanings, it may be wisest to follow Sidgwick[7] in referring to Lewis acids and bases as (electron)

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[7] N. V. Sidgwick, The Electronic Theory of Valency (Oxford University Press: 1929), in particular, p. 116 for the definition of donors and acceptors.
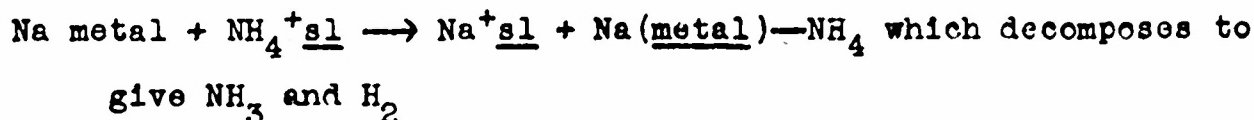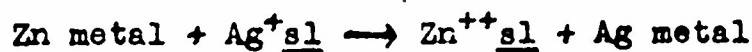

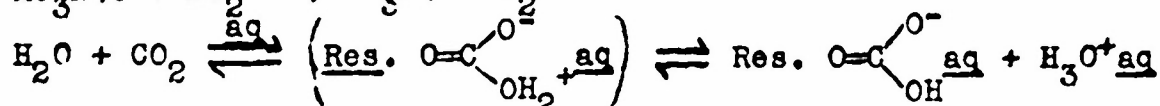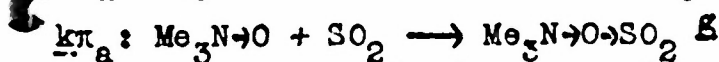acceptors and donors respectively.[8]

TABLE IV (CONTINUED)

8. Type $b\sigma + v^*$

$\underline{b\sigma_d}$: $MeEt_2CH + Me_2CH^+ \longrightarrow MeEt_2C^+ + Me_2CH_2$ $\underline{n}$

(Here in the $\underline{b\sigma_d}$ donor RQ, R is $MeEt_2C$, Q is H)

Zn metal $+ Ag^+\underline{sl} \longrightarrow Zn^{++}\underline{sl} + Ag$ metal

Na metal $+ NH_4^+\underline{sl} \longrightarrow Na^+\underline{sl} + Na(\underline{metal})$—$NH_4$ which decomposes to

give NH_3 and H_2

9. Types $\underline{n} + \underline{x\pi}$ and $\underline{n} + \underline{k\pi}$

$\underline{x\pi_a}$: $NH_3 +$ dinitrobenzene $\rightleftharpoons NH_3 \cdot$dinitrobenzene

$\underline{k\pi_a}$: $Me_3N{\rightarrow}O + SO_2 \longrightarrow Me_3N{\rightarrow}O{\rightarrow}SO_2$ $\underline{s}$

$H_2O + CO_2 \underset{\overrightarrow{aq}}{\rightleftharpoons} \left(\underline{Res.}\ O{=}C\overset{O}{\underset{OH_2}{\diagdown}}{}^+\ \underline{aq}\right) \rightleftharpoons Res.\ O{=}C\overset{O^-}{\underset{OH}{\diagdown}}\ \underline{aq} + H_3O^+\underline{aq}$
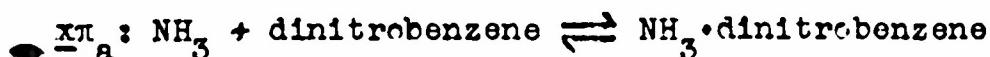
(or perhaps $CO(OH)_2$ is formed at once in the first step)

$\underline{k\pi_d}$: $NH_3 + RCHO \longrightarrow \left(RHC\overset{O^-}{\underset{NH_3}{\diagdown}}{}^+\right) \longrightarrow RHC\overset{OH}{\underset{NH_2}{\diagdown}}$
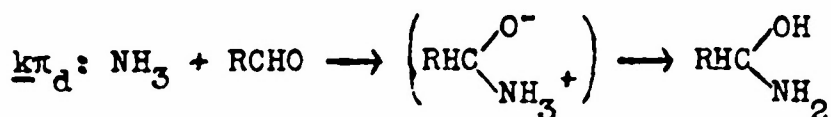
(In this and the first following, or probably both the follow-
ing, examples, the over-all process is of the type $\underline{b\sigma_d} + \underline{k\pi_d}$,
with an <u>intremolecular</u> $\underline{b\sigma_d}$ action. If the action proceeds in
a <u>single step</u>, it should be classified as $\underline{b\sigma_d} + \underline{k\pi_d}$.)

$H_2O + SO_3 \xrightarrow{aq} \left(Res.\ \overset{O}{\underset{O}{\diagup}}S\overset{O^-}{\underset{OH_2}{\diagdown}}{}^+\ \underline{aq}\right) \longrightarrow \overset{O}{\underset{O}{\diagup}}S\overset{OH}{\underset{OH}{\diagdown}}\ \underline{aq}$

$HCl + SO_3 \longrightarrow HCl{\rightarrow}SO_3$ or $ClSO_2OH$ (?) (chlorsulfonic acid) $\underline{o}$

10. Types $\underline{n'} + \underline{x\pi}$ and $\underline{n'} + \underline{k\pi}$

$\underline{x\pi_d}$: $MeO^-\underline{sl} + O_2N{-}\langle\ \rangle{-}OEt \xrightarrow{sl} Res. \left[\overset{O^-}{\underset{O}{\diagdown}}N^+{=}C\overset{CH{=}C}{\underset{CH{=}C}{\diagup}}\ ...\right]\underline{sl}$ $\underline{p}$
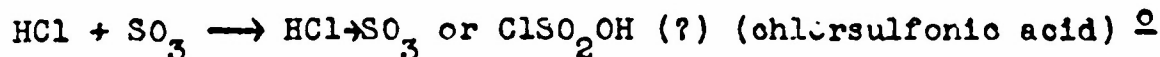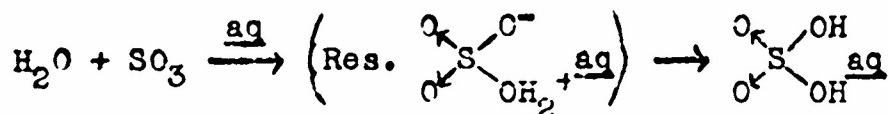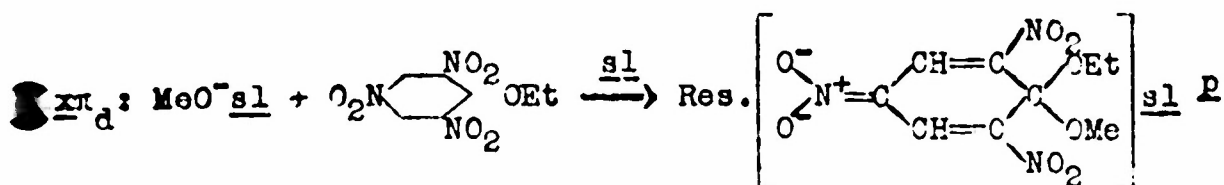
(in solution, with $\underline{sl} = \underline{es}$)

TABLE IV (CONTINUED)

$\underline{k\pi}_a$: $(Cl^- \cdot SO_2)\underline{sl}$ or $(Cl^- \twoheadrightarrow SC_2)\underline{sl}$

$\quad\quad$ ($\underline{sl}$ action on Cl^- partly $\underline{es}$, partly dative)

$\quad\quad$ $(Cl^- \cdot CH_3NO_2)\underline{sl}$ and $(Cl^- \cdot Me_2CO)\underline{sl}$ in nitromethane and acetone

$\underline{k\pi}_d$: $CN^-\underline{aq} + RCHO \longrightarrow \left(RHC \overset{O^-}{\underset{CN}{<}} \underline{aq} \right) \xrightarrow{H_3O^+\underline{aq}} RHC \overset{OH}{\underset{CN}{<}}$

$\quad\quad . \quad OH^-\underline{aq} + CO_2 \longrightarrow HCO_3^-\underline{aq}$

$\quad\quad Na^+Cl^-$ solid $+ SO_3 \longrightarrow Na^+[ClSO_3]^-$ solid

11. Types $\underline{b\pi} + \underline{x\pi}$ and $\underline{b\pi} + \underline{k\pi}$ [a]

$\underline{b\pi}_a \cdot \underline{x\pi}_a$: $PhNH_2 + s\text{-trinitrobenzene} \rightleftharpoons PhNH_2 \cdot s\text{-trinitrobenzene}$ $(\lambda4000)$[q]

$\quad\quad Bz + s\text{-trinitrobenzene} \rightleftharpoons Bz \cdot s\text{-trinitrobenzene}$ $(\lambda2800)$ [r]

$\underline{b\pi}_a \cdot \underline{k\pi}_a$: $MBz + SO_2 \rightleftharpoons MBz \cdot SO_2$ $(\lambda2840)$ [s]

$\quad\quad$ (MBz = various methylated benzenes)

$\quad\quad Bz + $ oxalyl chloride $\rightleftharpoons Bz \cdot$ oxalyl chloride $(\lambda2700?)$ [t]
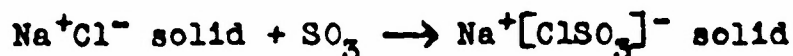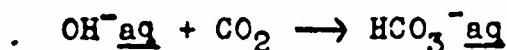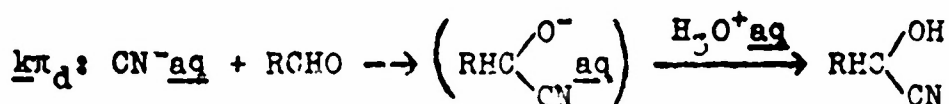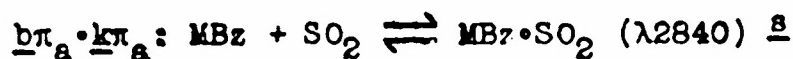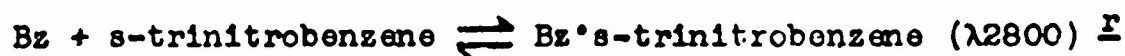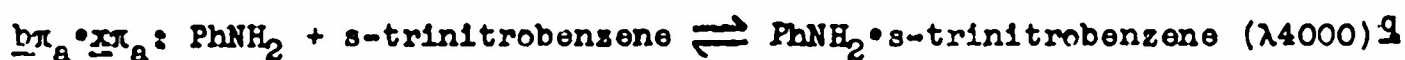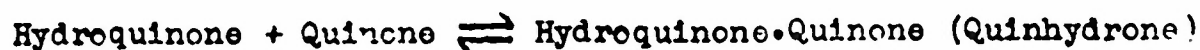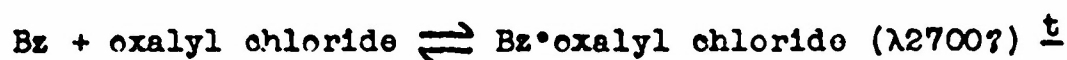
$\quad\quad$ Hydroquinone + Quinone $\rightleftharpoons$ Hydroquinone$\cdot$Quinone (Quinhydrone)
$\quad\quad$ (about $\lambda5600$ in crystal) [u]

12. Type $\underline{b\sigma}_d + \underline{k\pi}_d$
(see under $\underline{n} + \underline{k\pi}$, Part 9)

13. Type $\underline{n} + \underline{x\sigma}$

$\underline{x\sigma}_a$: t-butyl alcohol $+ I_2 \rightleftharpoons$ t-Bu-alcohol$\cdot I_2$ $(\lambda2330)$ [v]

$\quad\quad Et_2O + I_2 \rightleftharpoons Et_2O \cdot I_2$ $(\lambda2480)$ [v]

TABLE IV (CONTINUED)

$\underline{x}\sigma_a$ and $\underline{x}\sigma_d$: $Py + I_2 \rightleftharpoons Py\cdot I_2 \overset{slow}{\rightleftharpoons} [PyI]^+\underline{py} + I^-\underline{py};$ etc.^{w}

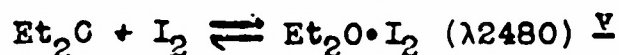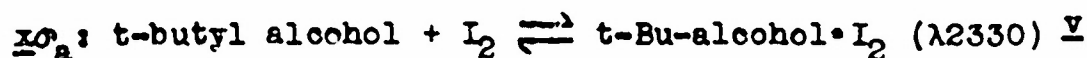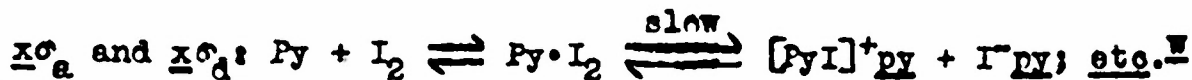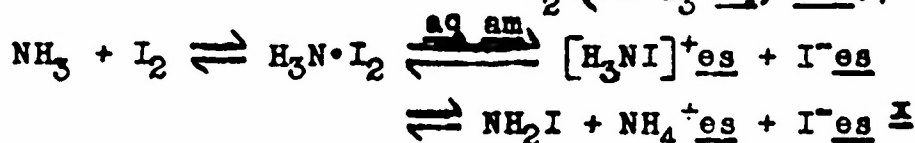(In pyridine solution. In $Py\cdot I_2$, Py may be acting as a **mixed** $\underline{n}$ and $\underline{b}\pi_a$ donor.)

$H_2O + I_2 \rightleftharpoons H_2O\cdot I_2 \overset{aq}{\rightleftharpoons} [H_2OI]^+\underline{aq} + I^-\underline{aq}$

$\overset{H_2O}{\rightleftharpoons} HOI + H_3O^+\underline{aq} + I^-\underline{aq}$ (and $I^-\underline{aq} +$ $I_2 \rightleftharpoons I_3^-\underline{aq}$, etc.)

$NH_3 + I_2 \rightleftharpoons H_3N\cdot I_2 \overset{aq\ am}{\rightleftharpoons} [H_3NI]^+\underline{es} + I^-\underline{es}$

$\rightleftharpoons NH_2I + NH_4^+\underline{es} + I^-\underline{es}$ ^{x}
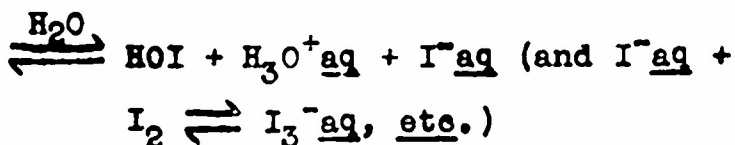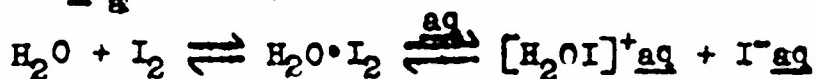
14. Types $\underline{n} + \underline{h}\sigma$ and $\underline{n} + \underline{k}\sigma$ ^{d}

$\underline{n}\cdot\underline{h}\sigma_a$ and $\underline{n}\cdot\underline{k}\sigma_a$: Theoretically, since almost certainly $E^{vert} \ll 0$ for HX (X = halogen) and probably for most HQ and RQ, it is very probable (cf. Sec. VI) that loose dative complexes of the type $\underline{n}\cdot\underline{h}\sigma_a$ and $\underline{n}\cdot\underline{k}\sigma_a$ in most cases do not exist. Loose electrostatic complexes, e.g., H-bonded complexes such as are observed for the D,A pairs $\underline{b}\pi,\underline{h}\sigma$ and $\underline{h}\pi,\underline{k}\sigma$--see under Type 19 in this Table--should, however, be possible under appropriate conditions. Formation of onium acids or salts ($\underline{h}\sigma_d$ or $\underline{k}\sigma_d$ behavior) usually (if not always) occurs only with $\underline{es}$ assistance ($\underline{h}\sigma_{ed}$ or $\underline{k}\sigma_{ed}$ behavior), either by formation of an ionic crystal or by solvation. For example, $NH_4^+Cl^-$ solid, and $NH_4^+\underline{sl} + Cl^-\underline{sl}$, are stable, but individual $NH_4^+Cl^-$ molecules in vapor (cf. W. H. Rodebush and J. C. Michalek, _J. Am. Chem. Soc._, **51**, 748 (1943); also footnote $\underline{y}$ below) or in inert solvents are apparently not stable (nor apparently is a loose complex $NH_3\cdot HCl$ appreciably stable). It may be, however, that individual salt molecules are in **some** cases stable without $\underline{es}$ assistance; for example, perhaps $Me_4N^+Cl^-$ and the like in benzene solution, and $[Me_2OH]^+Cl^-$
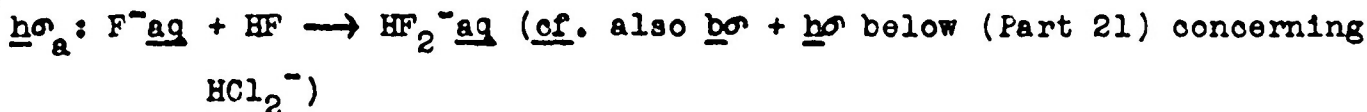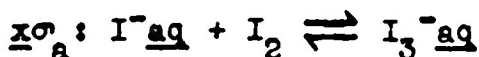
TABLE IV (CONTINUED)

in vapor (see Pfeiffer, p. 81 of reference in footnote a above) although here possibly the associated vapor molecules are of structure $Me_2O \cdot HCl$ of the $n \cdot k\sigma_a$ type (outer complex of Fig. 1 and Section IX).

$$\underline{h}\sigma_d: \quad H_2O + HCl \xrightarrow{\text{aq}} H_3O^+\underline{es} + Cl^-\underline{es} \quad (\underline{es} = \underline{aq})$$

$$H_2O + HBr \xrightarrow{\text{SO}_2} H_3O^+\underline{es} + Cl^- \cdot SO_2 \quad (\underline{es} = SO_2)$$

$$H_3N + HOH \underset{\text{slow}}{\overset{\text{aq}}{\rightleftharpoons}} NH_4^+\underline{es} + OH^-\underline{es} \quad (\underline{es} = \underline{aq})$$

$$H_3N + HCl \text{ (vapor)} \longrightarrow NH_4^+Cl^- \text{ (solid)} \quad X$$

$$\underline{k}\sigma_d: \quad Me_3N + MeCl \xrightarrow{\text{slow}} [Me_4N]^+Cl^- \text{ (slightly soluble solid)}$$

$$\text{(in Bz or PhNO}_2 \text{ solution)}$$

15. Type n + 1σ d

$$\underline{1}\sigma_d: \quad Me_2CO \rightarrow BCl_3 + Py \longrightarrow PyBCl_3 + Me_2CO$$

16. Types n' + xσ_a and n' + hσ_a

$$\underline{x}\sigma_a: \quad I^-\underline{aq} + I_2 \rightleftharpoons I_3^-\underline{aq}$$

$$\underline{h}\sigma_a: \quad F^-\underline{aq} + HF \longrightarrow HF_2^-\underline{aq} \text{ (cf. also } \underline{b}\sigma + \underline{h}\sigma \text{ below (Part 21) concerning } HCl_2^-)$$

17. Types n' + hσ_d and n' + kσ_d b

$$\underline{h}\sigma_d: \quad NH_2^-\underline{es} + HCPh_3 \longrightarrow NH_3 + CPh_3^-\underline{es}$$
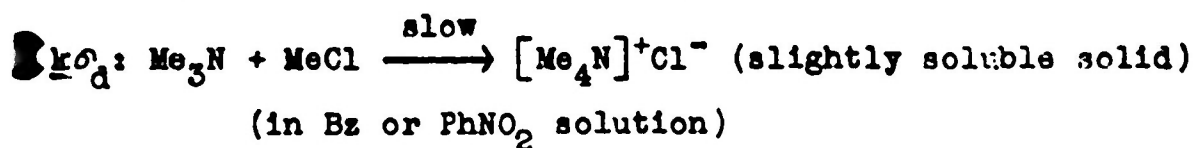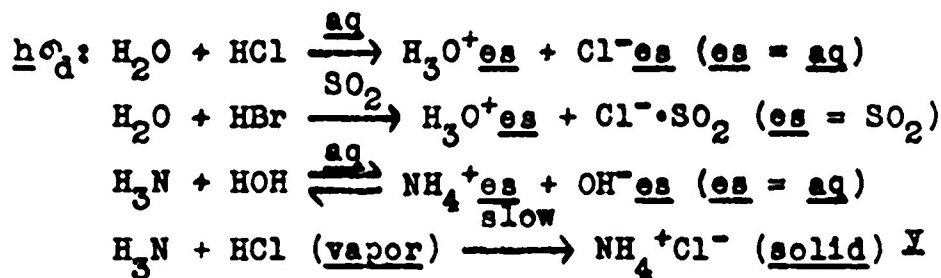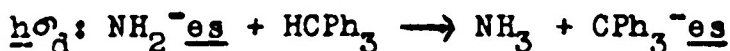
$$\text{(in liquid ammonia solution)}$$

$$EtO^-\underline{es} + HCH_2OOEt \rightleftharpoons EtOH + [CH_2OOEt]^-\underline{es}$$

$$\text{(in EtOH solution)}$$

$$\underline{k}\sigma_d: \quad \underline{aq} I^- + MeI \longrightarrow IMe + I^-\underline{aq}$$

$$\underline{aq}OH^- + MeI \xrightarrow{\text{slow}} HOMe + I^-\underline{aq}$$

TABLE IV (CONTINUED)

$$\underline{aq}Cl^- + CH_2{-}CH_2 \longrightarrow Cl{-}CH_2{-}CH_2{-}O^-\underline{aq} + HOH \longrightarrow Cl{-}CH_2{-}CH_2{-}OH$$

with the epoxide oxygen bridge on $CH_2{-}CH_2$

$$+ OH^-\underline{aq}$$

$$(\underline{n}') \qquad (\underline{k}\sigma_d) \qquad\qquad (\underline{n}') \qquad\qquad (\underline{h}\sigma_d)$$

18. Type $\underline{b}\pi + \underline{x}\sigma$

$\underline{b}\pi_a \cdot \underline{x}\sigma_a$: MBz $+ \overline{X}X \rightleftharpoons$ MBz$\cdot\overline{X}X$ ($\lambda 2900$) $\underline{Y}$
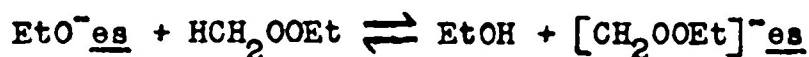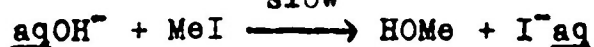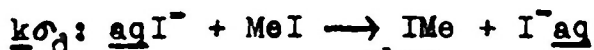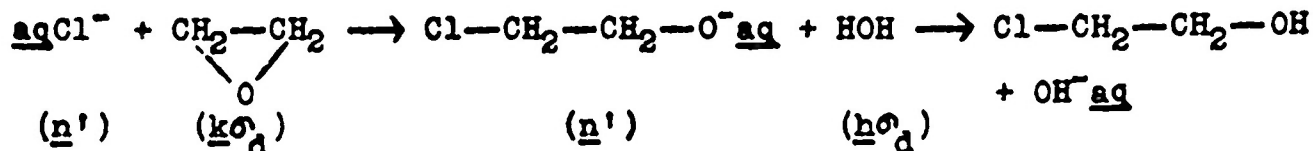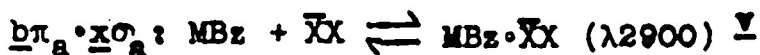
 (MBz = various methylated benzenes, $\overline{X}X$ = Cl_2, Br_2, I_2, ICl)

$$MC_2H_4 + I_2 \rightleftharpoons MC_2H_4{\cdot}I_2 \quad (\lambda 2700{-}3000) \; \underline{Z}$$
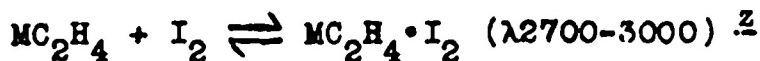
 (MC$_2$H$_4$ = various methylated ethylenes)

$$Bz + Ph_3CH \longrightarrow Bz{\cdot}Ph_3CH$$

$\underline{b}\pi_d + \underline{x}\sigma_d$: Bz $+ Cl_2 + FeCl_3 \longrightarrow ([BzCl]^+[FeCl_4]^-) \longrightarrow$ PhCl $+$ HCl $+$ FeCl$_3$

$$C_2R_4 + Cl_2 + AlCl_3 \longrightarrow ([C_2R_4Cl]^+[AlCl_4]^-)$$
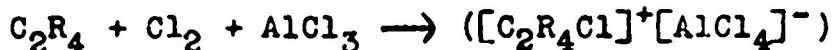
 (double charge transfer reactions of type $\underline{b}\pi_d + \underline{x}\sigma_d + \underline{v}$)

19. Types $\underline{b}\pi + \underline{h}\sigma$ and $\underline{b}\pi + \underline{k}\sigma$

$\underline{b}\pi_a \cdot \underline{h}\sigma_a$: There is evidence for loose complexes of the types $\underline{b}\pi_a \cdot \underline{h}\sigma_a$

 (e.g., methylated benzenes with HCl)[aa] and $\underline{b}\pi_a \cdot \underline{k}\sigma_a$ (e.g., Bz$\cdot$MeOH)[ab]
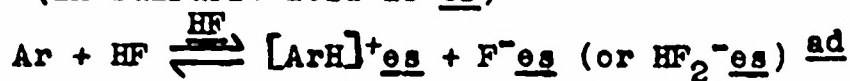
 These, however, are almost certainly members of a large class of

 weakly H-bonded es complexes,[ac] and not dative complexes. Presum-

 ably the H of MeOH or of HCl is attracted by the somewhat nega-

 tively charged carbons of the benzene ring (the C—H bonds have

 polarity C^-H^+). This would explain the increasing solubility with

 increasing methylation observed by Brown and Brady[aa] for HCl in

 MBz, since increasing methylation sends negative charge increas-

 ingly into the ring. Brown and Brady attribute the effect to in-

 creasing basicity, which would indeed give the same result, and

 which (interpreting basicity as meaning charge-transfer donor
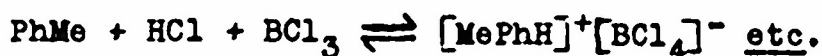
TABLE IV (CONTINUED)

strength) is indeed here believed responsible for the increasing stability with methylation of the superficially closely analogous MBz + X_2 complexes of type $\underline{b}x_a \cdot \underline{x}\sigma_a$; but it appears improbable that charge-transfer donor-acceptor interaction is appreciable for typical $\underline{h}\sigma$ and $\underline{k}\sigma$ acceptors without $\underline{es}$ solvent assistance (see remarks above under Types $\underline{n} + \underline{h}\sigma$ and $\underline{n} + \underline{k}\sigma$, Part 14).
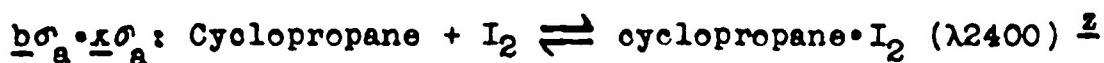
$\underline{b}\pi_d, \underline{h}\sigma_d$: $C_2R_4 + HHSO_4 \underset{}{\overset{es}{\rightleftharpoons}} [C_2R_4H]^+\underline{es} + HSO_4^-\underline{es}$

(in sulfuric acid as $\underline{es}$)

$Ar + HF \underset{}{\overset{HF}{\rightleftharpoons}} [ArH]^+\underline{es} + F^-\underline{es}$ (or $HF_2^-\underline{es}$) $\underline{ad}$

$Ar + HF + BF_3 \rightleftharpoons [ArH]^+\underline{es} + BF_4^-\underline{es}$

(in liquid HF as $\underline{es}$) $\underline{ae}$

$PhMe + HCl + BCl_3 \rightleftharpoons [MePhH]^+[BCl_4]^-$ etc.

(in toluene solution at low temperatures) $\underline{af}$

20. Type $\underline{b}\sigma + \underline{x}\sigma$

$\underline{b}\sigma_a \cdot \underline{x}\sigma_a$: Cyclopropane + $I_2 \rightleftharpoons$ cyclopropane$\cdot I_2$ ($\lambda 2400$) $\underline{z}$

21. Types $\underline{b}\sigma + \underline{h}\sigma$ and $\underline{b}\sigma + \underline{k}\sigma$

$\underline{b}\sigma_d, \underline{h}\sigma_a$: anisyl chloride + HCl $\longrightarrow$ (anisyl)$^+$ + HCl_2^- (?)

(in liquid HCl) $\underline{b}$

$\underline{b}\sigma_d, \underline{h}\sigma_d$: possibly (?) $NO_2OH + HHSO_4 \overset{es}{\longrightarrow} NO_2^+\underline{es} + HSO_4^-\underline{es} + H_2O$
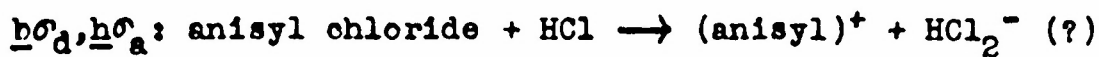
(in sulfuric acid as $\underline{es}$)

22. Type $\underline{n} + \underline{h}\sigma^{\#}$

$\underline{h}\sigma_d^{\#}$: $R_3N + H_3O^+\underline{aq} \longrightarrow [R_3NH]^+ + H_2O$

$H_2O + [H_2OI]^+\underline{aq} \longrightarrow H_3O^+\underline{aq} + HOI$ (cf. Type $\underline{n} + \underline{x}\sigma$, Part 13)
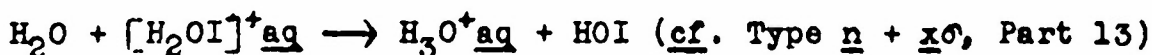
TABLE IV (<u>CONTINUED</u>)

23. Types $\underline{n}' + \underline{h}\sigma^{\#}$ and $\underline{n}' + \underline{k}\sigma^{\#}$

$\underline{h}\sigma_d^{\#}$: $MeCOO^- \underline{aq} + H_3O^+\underline{aq} \longrightarrow MeCOOH + H_2O$

$\underline{k}\sigma_d^{\#}$: $OH^-\underline{aq} + Me_3S^+\underline{aq} \longrightarrow MeOH + Me_2S$

24. Type $\underline{b}\sigma_d + \underline{k}\sigma_d^{\#}$

Ca metal + $COCl^+\underline{sl} \longrightarrow CO$ (from metal-CO?) + $Ca^{++}\underline{sl} + Cl^-\underline{sl}$

(in $COCl_2$ solution)
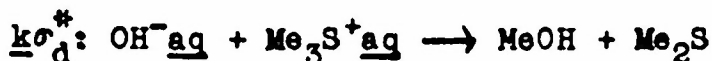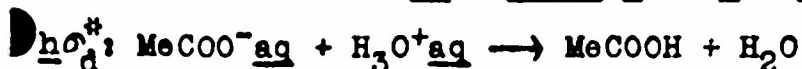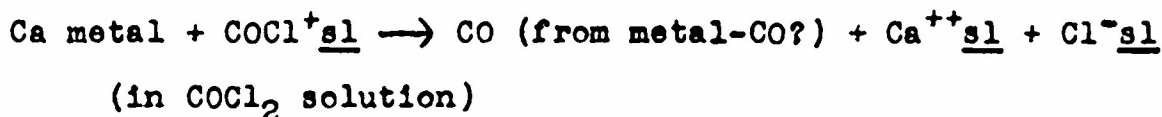
25. Some Types Involving R or Q

$R_n + \underline{v}^{\#}$: $H + H^+ \xrightarrow{sy} H_2^+$ (in gas)

$R_n + \underline{k}\sigma_d$: $Na + MeCl \longrightarrow Na^+Cl^- + Me$ (in gas)

$\underline{n}' + Q_v$: $Cl^- + Cl \xrightarrow{sy} Cl_2^-$ (in gas)

$\underline{b}\pi + Q_\sigma$: $MBz + Ph_3C \longrightarrow MBz \cdot Ph_3C$

(MBz = methylated benzenes)

$R_n + Q_v$: $Na + Cl \longrightarrow Na^+Cl^-$ (near $\lambda3000$) <u>ag</u>
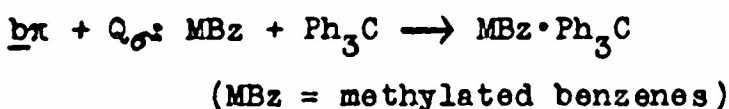
$R_n + R_n$: $H + H \longrightarrow H_2$ ($\lambda1010$) <u>ah</u>

$Q_v + Q_v$: $I + I \longrightarrow I_2$ ($\lambda1800$) <u>ah</u>

$R_n + Q_v$: $H + I \longrightarrow HI$ (est. $\lambda1280$) <u>ah</u>
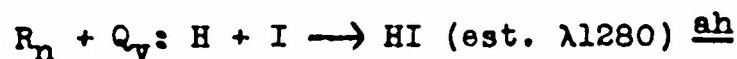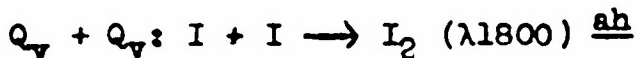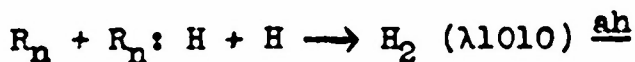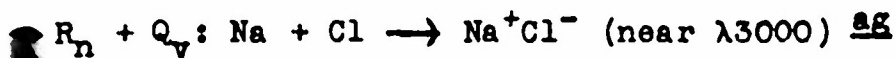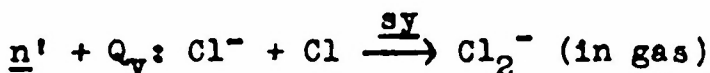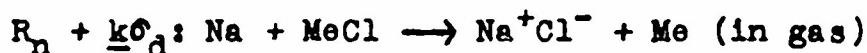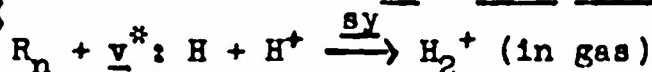
(These last four examples illustrate <u>interatomic</u> charge-transfer spectra.)

TABLE IV (CONTINUED)

FOOTNOTES

[a] For numerous examples of organic and organic-inorganic molecular complexes and compounds, mostly in the solid state, see P. Pfeiffer, *Organische Molekülverbindungen* (F. Enke: Stuttgart, 1927), 2nd edition.

[b] For references and discussion of a great many examples of donor-acceptor reactions and their mechanisms, see L. P. Hammett, *Physical Organic Chemistry* (McGraw Hill: 1940). For additional examples, see also Luder and Zuffanti, Ref. 6.

[c] The expression "*Res.*" means a mixture of equivalent structures of the type given.

[d] W. F. Luder (*J. Chem. Phys.*, **20**, 525 (1952)) describes on the one band the 1:1 reaction types $\underline{n}' + \underline{v}^*$ and $\underline{n} + \underline{v}$ as neutralization processes (*e.g.*, $CN^- + H^+ \longrightarrow HCN$ and $Me_2CC + BCl_3 \longrightarrow Me_2CO{\rightarrow}BCl_3$) and on the other hand the types $\underline{n} + \underline{h}\sigma_d$ and $\underline{n} + \underline{l}\sigma_d$ (*e.g.*, $HOH + HCN \longrightarrow H_3O^+ + CN^-$ and $Py + Me_2COBCl_3 \longrightarrow PyBCl_3 + Me_2CO$) as displacement processes, with H^+ and BCl_3 in the first pair regarded as primary Lewis acids, HCN and Me_2COBCl_3 in the second pair as secondary Lewis acids (*cf.* Section I for related comments).

[e] H. C. Brown, H. Pearsall, and H. P. Eddy, *J. Am. Chem. Soc.*, **72**, 5347 (1950).

[f] *Ibid.*, and H. C. Brown and H. Pearsall, *J. Am. Chem. Soc.*, **73**, 4681 (1951); R. L. Richardson and S. W. Benson, *loc. cit.*, **73**, 5096 (1951).

[g] A. B. Burg and W. E. McKee, *J. Am. Chem. Soc.*, **73**, 4590 (1951).

[h] Complexes of the type $\underline{b}\pi_a \cdot \underline{v}$ are apparently in general weak. Regarding $Ar \cdot AlX_3$, see R. E. Van Dyke, *J. Am. Chem. Soc.*, **72**, 3619 (1950).

[i] L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **73**, 5733 (1951).

[k] *Cf.* N. N. Lichtin and P. D. Bartlett, *J. Am. Chem. Soc.*, **73**, 5530

TABLE IV (CONTINUED)

FOOTNOTES (CONTINUED)

(1951).

[m] R. M. Keefer and L. J. Andrews, J. Am. Chem. Soc., 74, 640 (1952). For the toluene·Ag^+aq complex, Keefer and Andrews' analysis shows (1) an absorption peak near λ2650, of about double the intensity and at slightly longer wavelengths than a corresponding peak of toluene by itself; (2) rapidly rising intensity at shorter wave lengths toward a much more intense peak (not reached) which might lie at about λ2300. This second absorption is here tentatively identified as the charge-transfer (toluene→Ag^+) absorption. (Ag^+aq also shows a strong peak at somewhat shorter wavelengths, which may tentatively be identified with H_2O→Ag^+ charge-transfer.) In Ref. 2, Fig. 5 suggests that the (toluene→Ag^+) charge-transfer peak might be expected near λ3100. However, in constructing Fig. 5, previously existing estimates of the solvation energy of Ag^+ (see for example O. K. Rice, Electronic Structure and Chemical Binding (McGraw Hill: 1940): on p. 402 the solvation energy of Ag^+ in water is given as 106 kcal/mole) were overlooked. Making use of these, curve E of Fig. 5 would be raised by 1 or 2 ev (perhaps by 2 ev at large R and 1 ev at small R), and could very well be consistent with a charge-transfer peak near λ2300.

[n] P. D. Bartlett, F. E. Condon, and A. Schneider, J. Am. Chem. Soc., 66, 1531 (1944).

[o] Cf. H. H. Sisler and L. F. Audrieth, J. Am. Chem. Soc., 61, 3392 (1939) for references and studies on this and related examples.

[p] Branch and Calvin, The Theory of Organic Chemistry (Prentice-Hall: 1941), p. 481.

[q] J. Landauer and H. McConnell, J. Am. Chem. Soc., 74, 1221 (1952).

TABLE IV (CONTINUED)

FOOTNOTES (CONTINUED)

[r] H. McConnell and D. M. G. Lawrey, private communication.

[s] L. J. Andrews and R. M. Keefer, J. Am. Chem. Soc., 73, 4169 (1951).

[t] B. D. Saksena and R. E. Kagarise, J. Chem. Phys., 19, 994 (1951).

[u] See K. Nakamoto, J. Am. Chem. Soc., 74, 1739 (1952), on polarized-light spectra of this and other $b\pi_a \cdot k\pi_a$ complexes in solid state. (See text, Section II, for further details.)

[v] Regarding $Et_2O \cdot I_2$, cf. R. S. Mulliken, J. Am. Chem. Soc., 72, 600 (1950); 74, 811 (1952). In the first reference (p. 606), ε max for the λ2480 peak was in error; it should be 7760. Confirmed by recent work of J. S. Ham, extended also to (t-butyl alcohol)$\cdot I_2$ (see text, Section III).

[w] L. F. Audrieth and E. J. Birr, J. Am. Chem. Soc., 55, 668 (1933); R. A. Zingaro, C. A. Van der Werf, and J. Kleinberg, loc. cit., 73, 88 (1951). See also footnote v above.

[x] R. K. McAlpine, J. Am. Chem. Soc., 74, 725 (1952).

[y] As might be expected if this reaction goes only with es assistance (cf. discussion in text of table a few lines above), this reaction goes only slowly, presumably through a clustering mechanism which permits cooperative ion-pair formation (cf. E. L. Spotz and J. O. Hirschfelder, J. Chem. Phys., 19, 1215 (1951)).

[z] L. J. Andrews and R. M. Keefer, J. Am. Chem. Soc., 74, 458 (1952); S. Freed and K. M. Sancier, J. Am. Chem. Soc., 74, 1273 (1952). Various substituted ethylenes and butadienes, also (F and S) cyclopropane$\cdot I_2$.

[aa] H. C. Brown and J. Brady, J. Am. Chem. Soc., 71, 3573 (1949): solubilities of HCl in methylated benzenes. However, E. K. Plyler and D. Williams (Phys. Rev., 49, 215 (1936)) found but little shift in

8 For a valuable review, see R. P. Bell, Qu. Rov. Chem., 1, 113 (1947).

While Lewis's ideas grew largely out of inorganic chemistry, similar ideas were developed more or less independently in the field of organic chemistry, culminating in Lepworth's categories of anionoid and cationoid reagents, or Ingold's[9] of nucleophilic and electrophilic rea-

9 C. K. Ingold, Chem. Rev., 15, 225 (1934), especially pp. 265-273;
   J. Chem. Soc., 1933, 1120, especially the footnote on p. 1121.

gents. The latter correspond closely to Lewis's bases and acids, respectively, except that they add reducing agents rather generally to the former and oxidizing agents to the latter. Usanovich[10] also pro-

10 Usanovich in 1939 (see Ref. 6, p. 14, for a summary in English) defines an acid as any substance capable of giving up cations or of combining with anions, and a base as any substance capable of giving up anions or of combining with cations.

posed a similar classification. Luder and Zuffanti (Ref. 6, Chap. 4) elaborated an approach similar to Ingold's, but substituted the term "electrodotic" for Ingold's "nucleophilic". They stated that "both acids [primarily in Lewis's sense] and oxidizing agents are electron acceptors", and "are electrophilic [reagents]"; and that "both bases and reducing agents are electron donors" and "are electrodotic [reagents]".

In defining basic and acidic molecules, Lewis (although his essential idea seems to have been distinctly broader) emphasized as characteristic the sharing of an electron pair, furnished by the base and accepted by an atom in the acid. Sidgwick adopted the same definition for donors and acceptors.

TABLE IV (CONTINUED)

FOOTNOTES (CONTINUED)

the HCl infrared fundamental for benzene solutions as compared with HCl vapor, whereas for other solvents (e.g., nitrobenzene, ethers) large shifts were found: W. Gordy and P. C. Martin, J. Chem. Phys., 7, 99 (1939).

ab L. H. Jones and R. M. Badger, J. Am. Chem. Soc., 73, 3132 (1951).

ac Work by many authors. Some recent papers including key references to earlier papers are: S. Searles and M. Tamres, J. Am. Chem. Soc., 73, 3704 (1951), and references on infrared spectra in footnotes aa and ab.

ad Klott, Z. anorg. allegem. Chemie, 234, 189 (1937). M. Kilpatrick, unpublished work.

ae D. A. McCaulay and A. P. Lien, J. Am. Chem. Soc., 73, 2013 (1951). M. Kilpatrick, unpublished work.

af H. C. Brown and H . W. Pearsall, J. Am. Chem. Soc., 74, 191 (1952).

ag Cf. R. S. Mulliken, Phys. Rev., 51, 327 (1927).

ah Cf. R. S. Mulliken and C. A. Rieke, Reports on Progress in Physics (London Physical Society), 8, 249 (1941).

III. LOOSE MOLECULAR COMPLEXES IN THE SOLID STATE

The structure of any loose 1:1 molecular complex or compound between neutral closed-shell entities can be described in terms of wave-functions essentially as follows:[2]

$$\psi_N \approx a\psi_0(B,A) + b\psi_1(B^+\!\!-\!A^-) , \tag{1a}$$

where $\psi_0(B,A)$ represents a no-bond structure and $\psi_1(B^+\!\!-\!A^-)$ a dative structure for the donor-acceptor pair B,A. A more general expression not limited to neutral closed-shell entities has already been given at the beginning of Section I (Eq. (1)).

Eq. (1a) is easily generalized to cover n:1 and other cases.[2] The fact that solid crystals are abundantly known[12] with the same 1:1

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[12] P. Pfeiffer, Organische Molekülverbindungen (F. Enke: Stuttgart, 1927), 2nd edition.

(or in general m:n) composition as for individual molecules of complexes in solution or in vapor can also be understood. It is only necessary to assume that even in such a crystal (the same applies also to an n:1 or m:n complex) the predominant intermolecular forces are local, pair-wise, donor-acceptor interactions between each donor molecule and its nearest acceptor neighbors, and between each acceptor molecule and its nearest donor neighbors. This assumption is quantum-mechanically entirely reasonable, and it appears safe to take the fact of the very frequent occurrence of complexes in solution and as crystalline solids with the same stoichiometric composition, as very strong empirical evidence of its correctness. Further evidence from the spectra of solid complexes will be reviewed in Section IV. Cooperative effects involving more remote neighbors (and finally the entire crystal) must also of course exist, but apparently these are of secondary importance in

typical cases.

As has been pointed out previously,[2,3] donor-acceptor inter-
actions, even though relatively weak, should exist also in molecular
crystals built from a single molecular species, and often these forces
should have orientational properties. In particular, they should tend
to cause aromatic molecules to be stacked in such a way that the planes
of adjacent molecules, although parallel, are displaced from being
directly superposed.[13] This is what is observed in the crystals both

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[13] Ref. 2, Secs. VII, VIII; and J. Landauer and H. McConnell, J. Am.
   Chem. Soc., 74, 1221 (1952).

---

of aromatic molecules of a single species and of aromatic molecular com-
plexes. Such molecules are often stacked like a pack of cards along an
axis, but with the planes of the molecules all inclined to the stacking
axis.[14] Examples of the two cases are the crystals of hexamethylbenzene

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[14] K. Nakamoto, J. Am. Chem. Soc., 74, 390, 392, 1739 (1952). These
   papers include a convenient brief survey of several examples illus-
   trating the modes of packing of aromatic molecules in crystals.

(stacking angle $44^\circ 27'$) and quinhydrone (1:1 quinone-hydroquinone;
stacking angle 34°). On the other hand, for the crystals of $(CH_2Br)_6C_6$
(hexabromomethylbenzene) the molecules are strung directly above one
another along the axis (stacking angle 0°). This is understandable on
the basis of steric effects: the bromine atoms are so big as to keep
the benzene planes much farther apart than in hexamethylbenzene. One
may then suppose that the charge-transfer orientational forces are large
enough in the latter, but too small in $(CH_2Br)_6C_6$, to cause stacking at
an angle. This explanation should, however, be considered for the pre-
sent as tentative.

IV. CHARGE-TRANSFER SPECTRA

As has been pointed out previously,[2] if Eq. (1a) represents the ground state $\underline{N}$ of a 1:1 molecular complex, there must also exist an excited state $\underline{E}$ with

$$\psi_E \approx a\psi(D^+\!-\!A^-) - b\psi(D,A) . \tag{4}$$

Then if, for example, the ground state has predominantly no-bond structure ($\underline{a}^2 \gg \underline{b}^2$), this excited state must have predominantly dative structure. It was also pointed out that on the basis of quantum mechanics the absorption spectrum of the complex must include (in addition to the individual spectra of D and A, somewhat modified by their interaction) a band (normally in the visible or ordinary ultraviolet) corresponding to an absorption jump from state $\underline{N}$ to state $\underline{E}$, and characteristic of the complex as a whole. This was called an intermolecular charge-transfer spectrum. Especially notable is the fact that the theory predicts the possibility of highly intense charge-transfer absorption even for very loose complexes.[2]

As a prime example, the intense absorption near λ2900 in the spectra of the loose complexes of benzenoid hydrocarbons with molecules of the halogens was discussed in detail in Ref. 2. Tentative identification of an intense ultraviolet absorption of solutions of iodine in ethyl ether as being a charge-transfer spectrum of an ether-iodine complex was also made.[4] Unpublished work just completed by Mr. J. S. Ham in this laboratory, showing that this spectrum definitely belongs to a 1:1 ether-iodine complex, supports this view. Mr. Ham has also measured a new ultraviolet absorption in the spectrum of solutions of iodine in t-butyl alcohol, and identified it as a charge-transfer spectrum of a 1:1 complex.

During the past year, other investigators (especially Andrews and Keefer) have published several papers on molecular complexes and their spectra, in which equilibrium constants were determined and which revealed the possible or probable presence of charge-transfer spectra. The wavelengths of a number of such spectra are listed under the appropriate complexes in Table IV, together with literature references. In many cases, the charge-transfer identification was mentioned tentatively by the authors of the papers cited.

In addition, there are numerous less recent papers on organic complexes in which color changes have been noted, and a few for which spectra have been mapped. Further, attention should be called to the absorption spectra of inorganic complexes and ions in solution and in crystals, a subject briefly reviewed by Rabinowitch in 1942.[15] Most

[15] E. Rabinowitch, Rev. Mod. Phys., 14, 112 (1942). Review on electron-transfer and related spectra.

of the spectra of stable complex anions such as NO_3^-, CH_3COO^-, MnO_4^-, and of complex cations of similar stability, may best be considered as normal molecular spectra, but it may be noted that normal molecular spectra include interatomic charge-transfer spectra.[16] In addition,

[16] R. S. Mulliken, J. Chem. Phys., 7, 201 (1939) and later papers, especially R. S. Mulliken and C. A. Rieke, Reports on Progress in Physics (London Physical Society), VIII, 231 (1941).

anions in solutions, in particular simple ions like Cl^-, contain spectra which have long been attributed to electron transfer from the anion to environning molecules, but to which Platzmann and Franck have recently given an interesting new and rather different interpretation.[17] Earlier

[17] R. Platzmann and J. Franck, L. Farkas Memorial Volume.

(1926), Franck and collaborators had shown that the absorption spectra of alkali halide vapors correspond to an interatomic electron transfer process. Still earlier, the concept of electron transfer was used in interpreting the spectra of ionic crystals.[15] The high-intensity short wavelength absorption spectra of many of the less stable cations and anions in solution have been described by Rabinowitch as electron transfer spectra.[15]

In the earlier work, it was supposed that electron transfer spectra occur only corresponding to transfer of an electron from a negative ion (or perhaps an electron donor like H_2O--cf. Table V of Ref.15) to a positive ion. The more recent work[16,2] corresponds to a broader concept in which electron transfer spectra may occur corresponding to electron transfer between any two atomic or molecular entities, even if these are uncharged. It appears probable that a re-examination of the structure and spectra of complex ions from the present point of view will be very fruitful.

Returning to the organic complexes, a recent paper by Nakamoto[14] is of particular interest. Nakamoto examined long wavelength spectra which appear to be the charge-transfer spectra of certain 1:1 crystalline molecular complexes (among others, quinone: hydroquinone), in polarized light. For 1:1 complexes between aromatic or unsaturated π donors and π acceptors, the theory[2] predicts that the electric vector should be polarized perpendicular to the planes of the two molecules (which should be parallel to each other), and this is what Nakamoto found. As was pointed out in Section III, it is reasonable to suppose that the charge-transfer forces in such crystalline complexes act essentially pairwise between neighboring molecules. The spectra should then be similar to those for individual 1:1 complexes in solution, although appreciably modified by cooperative effects involving non-neighbor

molecules. Thus Nakamoto's work appears both to confirm the charge-transfer interpretation of the characteristic spectra of molecular complexes, and to support the idea of primarily pairwise-acting charge-transfer forces in crystalline complexes.

A further point of interest is that in aromatic crystals composed of a single molecular species (e.g., hexamethylbenzene), although the stacking of the molecules at an angle to the stacking axis (cf. Section III above) is explainable by charge-transfer forces (and no other explanation is evident), there is in the longer wavelength part of the spectrum no charge-transfer absorption band like that for quinone-hydroquinone. This is theoretically not unreasonable, since for self-complexes[13] the charge-transfer forces should be much weaker, and the charge-transfer absorption in general much weaker and at shorter wavelengths, than for the much stronger complexes between unlike molecules. Whether, however, the existence of sufficiently strong charge-transfer forces to account for the stacking of the molecules of a self-complex at a considerable angle is quantitatively compatible, in terms of theory, with the absence of any indication of a charge-transfer spectrum, is a matter which should be investigated further. Meantime, it may be useful to assume this compatibility at least as a guiding hypothesis in further experimental studies.

V. THE STRENGTHS OF DONORS AND ACCEPTORS

The factors determining the strengths of donors and acceptors in the formation of relatively loose addition complexes have been discussed previously.[2] The importance of low vertical ionization potentials I^{vert} for strong donors, and of high vertical electron affinities E^{vert} for strong acceptors, was stressed. It was pointed out that I^{vert} and E^{vert} should be taken corresponding to a nuclear skeleton which is that of the actual complex. This is a compromise (often a severe one)

between the often very different skeletal structures that would occur for molecules with electronic structures corresponding to the separate resonance components ψ_0 and ψ_1 of Eq. (1a). The importance of other factors, in particular mutual approachability, in determining interaction strengths, was also emphasized. For example, approachability is especially good between $\underline{n}$ (or $\underline{n}'$) donors and $\underline{v}$ (or $\underline{v}^*$) acceptors, or between π donors and π acceptors, but not between π donors and $\underline{v}$ acceptors.

When donors and acceptors interact not in the associative but in the dissociative mode, the factors determining donor and acceptor strengths are altered considerably. Leaving aside entropy factors for the moment, the important factors can be seen by writing equations for the various terms involved in the net heat of reaction. For ionogenic displacement reactions like (3), one immediately finds that low $\underline{I}$ (here not $\underline{I}^{vert}$) values are favorable for good donors, and high $\underline{E}$ (not $\underline{E}^{vert}$) for good acceptors.

Specifically, for the reaction of an associative donor D with a dissociative σ acceptor RQ,

$$D + RQ + \underline{sl} \longrightarrow DR^+\underline{sl} + Q^-\underline{sl} , \tag{3a}$$
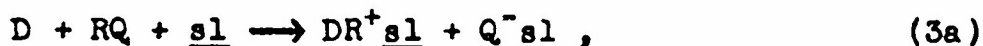
the heat of reaction is evidently

$$\left. \begin{array}{l} E_Q + H_{Q^-} + H_{DR^+} + (D_{DR^+} - D_{RQ}) - I_D \\[2mm] = (H_{DR^+} + D_{DR^+} - I_D) + (H_{Q^-} - D_{RQ} + E_Q) . \end{array} \right\} \tag{3b}$$

Similarly, for the reaction of a dissociative σ donor RQ with an associative acceptor A (e.g., a $\underline{v}$ acceptor),

$$RQ + A + \underline{sl} \longrightarrow R^+\underline{sl} + QA^-\underline{sl} , \tag{3c}$$

the heat of reaction is

$$E_A + H_{R^+} + H_{QA^-} + (D_{QA^-} - D_{RQ}) - I_R$$

$$= (H_{R^+} - D_{RQ} - I_R) + (H_{QA^-} + D_{QA^-} + F_A) .$$

(3d)

In Eqs. (3b) and (3d), it is not I_D^{vert} and E_A^{vert} which matter, but I_D and E_Q in the former, I_R and E_A in the latter. The difference between the energy of the bond which is formed and that which is broken also plays a part, but often one of minor importance. It is easily seen why solvation of the ions is so often the decisive factor in making iono-genic reactions possible. High bond and solvation energy for the ca-tion formed from the donor (e.g., NH_4^+ from NH_3) are here favorable for high donor strength; and low dissociation energy for the acceptor (e.g., HCl) and high solvation energy for the anion formed from it (e.g., Cl^-) are favorable for high acceptor strength.

As stressed by Lewis,[5] it is not feasible to arrange bases and Lewis acids into unique orders of strength valid for all Lewis acid-base reactions. It is usually concluded as a corollary that it is futile to try to arrange acids or bases in any universally valid quantitative or-der of strength, except for acid and base strengths in the familiar case of H-acids interacting with bases in solutions. However, with the present classification of donors and acceptors into a number of fairly well-marked types, perhaps it will be worth while to see whether roughly quantitative scales of donor and acceptor strength can be set up for the interactions of donors of a particular type with acceptors of a particu-lar type; and then to look for different scales for other pairs of types.

VI. CONDITIONAL AND UNCONDITIONAL DONOR AND ACCEPTOR BEHAVIOR[18]

18 For a general survey of reaction rates and mechanisms, especially in solution, reference may be made to L. P. Hammett, Physical Organic Chemistry (McGraw Hill: 1940), and to Glasstone, Laidler, and Eyring,

The Theory of Rate Processes (McGraw Hill: 1941).

Beyond the classifications given in Tables III and IV, donor-acceptor reactions may be characterized as either unconditional or absolute (occurring between the members of the donor-acceptor pair without assistance, for example, in vapor or in inert solvents); or as conditional or contingent (requiring the presence of environmental cooperation).

Environmental cooperative action[19] may take various forms,

[19] See also E. D. Hughes' discussion (Trans. Faraday Soc., 34, 185 (1938)) of "constitutional effects..." and "environmental effects in nucleophilic substitution".

among which it will be convenient to distinguish two principal cases. One of these, designated "es" in Tables I-IV (see footnote c of Table I), is that of essentially electrostatic environmental action. In the other, two molecules of solvent and/or solute cooperate in reacting as donors or acceptors with a third molecule (for examples, see Tables III, IV).

Usually "es" involves definite attachment to the donor-acceptor reaction product of solvent molecules (solvation, usually with dissociation into solvated ions) or else polymerization (formation of ion-clusters in solution, or of an ionic crystalline solid). The role of es in conditional reactions is to stabilize the reaction products sufficiently to make the reaction possible.

The principal dissociatively functioning types of donors ($\underline{b}\pi_d$, $\underline{b}\sigma_d$ donors) and of acceptors (π_d, σ_d, and σ_d^* acceptors) seldom function dissociatively without environmental cooperation. Donors and acceptors subject to this limitation may properly be grouped together under the name of conditional dissociative donors and acceptors.

Ingold[9] said: "reagents which donate their electrons to, or share them with, a foreign atomic nucleus may be termed nucleophilic"; those "which acquire electrons, or a share in electrons, previously belonging to a foreign molecule or ion, may be termed electrophilic". Luder and Zuffanti (loc. cit.) stated that "an acid accepts a share in an electron pair held by a base; an oxidizing agent takes over completely the electrons donated by a reducing agent," and made a corresponding statement regarding bases and reducing agents. It is proposed here to use Sidgwick's simple and almost self-explanatory terms "donor" and "acceptor" to mean essentially the same things as Ingold's "nucleophilic reagent" and "electrophilic reagent", or Luder and Zuffanti's "electrodotic reagent" and "electrophilic reagent".

More precisely, (electron) donors D and acceptors A are here defined as all those entities such that, during the interaction between a particular species of D and a particular species of A entities, transfer of negative charge from D to A takes place, with the formation as end-products either of additive combinations or of new entities; the additive combinations may be 1:1, m:1, 1:n, or in general m:n combinations.

This definition is one which becomes extremely natural when one attempts to express the familiar ideas of donor-acceptor interaction in quantum-mechanical symbols.[2] The wave-function ψ of the (stable or transitory) 1:1 complex A·D then takes in general the approximate form

$$\psi \approx a\psi_0(AD) + b\psi_1(A^-D^+) , \qquad (1)$$

with appropriate ionic or covalent bonding (or no bonding) between D and A, and between A^- and D^+, depending on whether A and/or D are closed-shell molecules or ions.

It will be noted that the terms "conditional" and "uncondi-tional" describe alternative modes of functioning of donors and accep-tors, just as do the terms "dissociative" and "associative", introduced in Section II and Tables I-IV and indicated there by subscripts d and a. It would therefore be appropriate to add further subscripts, say c and u, for conditional and unconditional modes respectively, leading to symbols such as x^σ_{ua}, x^σ_{cd}, h^σ_{cd}, etc. In most cases, however, only one of the alternatives u or a occurs for any one donor or acceptor class and subclass, and so these subscripts have been omitted in the symbols in Tables I-IV. Nevertheless under some circumstances, to in-dicate special types of conditional functioning, it may prove useful to employ subscript symbols. Symbols such as x^σ_{cd}, $x^\sigma_{es,d}$, x^σ_{vd}, $x^\sigma_{sl,d}$, $x^\sigma_{xt,d}$, are therefore suggested to denote, respectively, conditional functioning of unspecified character, of electrostatic character, of auxiliary v-acceptor character, of solvent character (pure es, donor or acceptor, or mixed, in nature), and ionic-crystal-es character; with at the same time dissociative functioning in all.

It should further be noted that the n' donors and the $v^\#$ and $d^\#$ acceptors, being ionic, are seldom encountered except under es condi-tions. However, in Tables I and II, this fact has been embodied in the usual definitions of these types. For example, the anionic chlorine donor is defined as Cl^-es, which may mean Cl^- surrounded by Na^+ (and so on) in a crystal, or attached to a single Na^+ in vapor or in an inert solvent, or hydrated Cl^- (Cl^-aq) in water solution. With these defini-tions, n' donors and $v^\#$ and $d^\#$ acceptors are here regarded as uncondi-tional.

A further point is that the "es" in an n' donor or $v^\#$ acceptor is intended in general to have qualitative rather than quantitative mean-ing, so that, for example, it is not necessary to account for a fixed

number of water molecules when a Cl^-_aq_ donor reacts.

Still another related point is the fact that when an ion is solvated, the solvating solvent molecules may function either in a purely _es_ role as discussed in the two preceding paragraphs, or in a more or less strongly donor or acceptor role, as for example, the two NH_3 in $Ag^+(NH_3)_2$_aq_, and the SO_2 in Cl^-SO_2. If the solvent molecules function definitely as donors or acceptors, they are conceived of here as forming integrated structural parts of larger entities, such as, for example, the $\sigma_d^{\#}$ acceptor $Ag^+(NH_3)_2$_aq_, or the $\sigma_d^!$ donor Cl^-SO_2. In practise, of course, border-line cases are frequent. In such cases, it may be best to be guided by convenience, and to some extent custom, even at the risk of arbitrariness. For example (_cf_. Table IV), Ag^+_aq_ is most conveniently regarded as a $\underline{v}^{\#}$ acceptor, rather than as a $\sigma_d^{\#}$ acceptor like $Ag^+(NH_3)_2$_aq_, even though it may be that the $\sigma_d^{\#}$ classification would be closer to the truth. Similarly, Cl^-SO_2 may often conveniently be regarded like Cl^-_aq_ as an $\underline{n}^!$ rather than a $\sigma_d^!$ donor. On the other hand, it is probably unwise to class the typical stable $\sigma_d^{\#}$ acceptor H_3O^+_aq_ as a $\underline{v}^{\#}$ acceptor (H^+_aq_).

Conditional σ_d acceptors (σ_{cd} acceptors) like HQ or RQ are, _as such_, strictly speaking, not acceptors or Lewis acids at all; it is really not they, but HQ plus _es_ or RQ plus _es_, which function as σ_{cd} acceptors. The usual omission of reference to _es_ may be considered as a convention adopted in the interest of simplicity. It is particularly important to remind oneself of this when using the ordinary concept of H-acids, a concept of whose very existence this tacit convention is an intrinsic part.

Some types of donors and acceptors typically function only unconditionally, and others only conditionally. Acceptors of the $\underline{x}\sigma$ subclass, however, although unconditional when functioning associatively

($\underline{x}\sigma_{ua}$ acceptors), often act in the presence of ionizing solvents as conditional acceptors ($\underline{x}\sigma_{od}$ acceptors). Thus if iodine is dissolved in water, it seems probable that unconditional formation of the loose reversible $\underline{n}\cdot\underline{x}\sigma_a$ complex $H_2O\cdot I_2$ first occurs, very rapidly; and that then, with the $\underline{es}$ assistance of water, reaction occurs over an activation barrier to a structure $H_2OI^+I^-$ (of $\underline{n}\to\underline{x}\sigma_d$ type), thence to $H_2OI^+\underline{es}$ + $I^-\underline{es}$; whereupon the $\sigma_d^{\#}$ acceptor $[H_2OI]^+$ is attacked by the $\underline{n}$ donor H_2O to form $HOI + H_3O^+\underline{aq}$; and so on. There seems to be evidence that in this complex and reversible series of donor-acceptor reactions, the iodine is present predominantly as $H_2O\cdot I_2$. In the example just discussed, it will be noted that the water acts sometimes in an $\underline{es}$ role, sometimes as an $\underline{n}$ donor.

VII. DETAILED COMPARISON OF DISSOCIATIVE AND ASSOCIATIVE DONOR-ACCEPTOR REACTIONS

To clarify further the brief comparison in Section I between associative and dissociative charge-transfer reactions, it is instructive to follow each of the reactions Eqs. (2) and (3) through from beginning to end in terms of a varying linear combination of two resonance structures ψ_0 and ψ_1 of the kind specified in Eq. (1a). In both reactions, $\underline{a}$ of Eq. (1a) decreases and $\underline{b}$ increases as the reaction proceeds. To make matters fully clear, additional details are needed to describe the metamorphoses, during reaction, of the internal structures of the original donor and acceptor in ψ_0 and of their ions in ψ_1.[11,19]

For reaction (3), Eq. (1a) becomes

$$\psi_N \approx a\psi_0(H_2O, HCl) + b\psi_1(H_2O^+\underset{aq}{-\!\!-\!\!-}HCl^-) . \qquad (4)$$

Here the formulation in terms of HCl^- is admittedly artificial, especially since $E^{vert} \ll 0$ in the first stages of the reaction (see Table IV, discussion under reaction-type 14). Actually, with detailed resonance

structures given as in (5) below, no mention of HCl⁻, or of ψ_0 or ψ_1, is really essential. However, the introduction of the concepts which these represent is valuable in showing the parallelism between reactions (2) and (3).

Neglecting some minor resonance structures, and leaving to be tacitly understood the presence and *es* action of the solvent, reaction (3) must go somewhat as follows:

$$\psi(H^{+\cdot4}H^{+\cdot4}O^{-\cdot8},\ H^{+\cdot2}Cl^{-\cdot8}) = \psi_0(H_2O,\ HCl) =$$

$$\psi_0 : \begin{cases} \underline{0.8}\ H_2O,\ \ldots\ldots H\!\!-\!\!Cl \\ \underline{0.2}\ H_2O,\ \ldots\ldots H^{\overset{+}{\cdot}}\ldots Cl^- \end{cases} \longrightarrow$$

$$\left\{ \begin{array}{l} \psi_0 : \begin{cases} \underline{.39}\ H_2O \longleftrightarrow H\!\!-\!\!Cl \\ \underline{.35}\ H_2O\ldots..H^{\overset{+}{\cdot}}\ldots..Cl^- \end{cases} \\ \psi_1' : \begin{cases} \underline{.25}\ H_2O^{\overset{+}{\cdot}}\!\!-\!\!H\longleftrightarrow Cl^- \\ \underline{.01}\ H_2O^{\overset{+}{\cdot}}\ldots.H^{\overset{-}{\cdot}}\longleftrightarrow Cl \end{cases} \end{array} \right\} \longrightarrow \qquad (5)$$

$$\begin{cases} \underline{.5}\ \psi_0 : H_2O\ldots H^+,\ \ldots\ldots Cl^- \\ \underline{.5}\ \psi_1' : H_2O^{\overset{+}{\cdot}}\!\!-\!\!H\ ,\ \ldots\ldots Cl^- \end{cases} =$$

$$\psi(H^{+\cdot5}H^{+\cdot5}O^{-\cdot5}H^{+\cdot5},\ \ldots\ldots Cl^{-1}) = \psi(H_3O^+,\ \ldots\ldots Cl^-) = \psi\left[(H_2O)^{+\cdot5}(HCl)^{-\cdot5}\right].$$

The numbers preceding the individual resonance structures are rough estimates of their relative weights. The symbols —, ..., and ⟷ indicate covalent bonding, electrostatic attraction, and nonbonded repulsion respectively. The first and last lines contain various types of summary of the estimated detailed charge distributions in the initial and final stages.[20]

The structure $H_2O...H^{\pm}-Cl$, with estimated coefficient only 0.01 in the intermediate stage in (5), is mentioned here since, although unimportant in this example, analogous structures should be of considerable importance in general (for example, in $H_2O + I_2$ and other $\underline{n} + \underline{x}\sigma_d$ reactions (cf. Table IV)).

A comparison between various formulations of the initial and final stages in (5) permits various descriptions of the over-all effects of the reaction. One point which is interesting (to the extent that the estimates are correct) is that although the H_2O molecule as a whole donates 0.5e to (the two parts of) the HCl, the O atom in H_2O donates only 0.3e of this, and moreover still remains negatively charged in the final ion H_3O^+. Also, the Cl atom, in attaining its final charge of -1.0e, starts with -0.2e taken from its original partner, picks up a further -0.3e from this partner during the action, and gains -0.5e more from the original H_2O, of which the O supplies -0.3e and the two hydrogens each -0.1e.
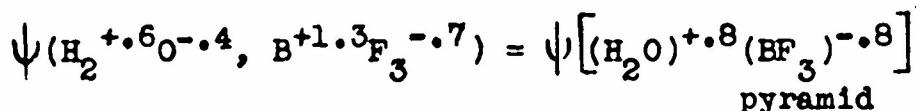
In scheme (5), the intermediate stage shown probably represents an activated state. In an analogous formulation of some of the other reactions in Table IV (see in particular reaction-types 13, 14, and 17 there), the intermediate stage certainly corresponds to an activation barrier over which the reaction proceeds slowly (rate measurements have been made in many examples). The fact that reactions such as (3) do not go in the vapor phase (cf. Table IV, footnote y) probably means that without solvent or crystallization assistance the final stage of the reaction in which ions are definitely formed, although doubtless lower in energy than the intermediate activated state, would be higher in energy than the initial stage before reaction. The way in which the energy varies with degree of reaction would then correspond to curve I

in Figure 1, below.

For comparison with (5), a similarly formulated description of the initial and final stages of reaction (2) is given in (6). Again the reader is warned that the estimated numbers are very uncertain.
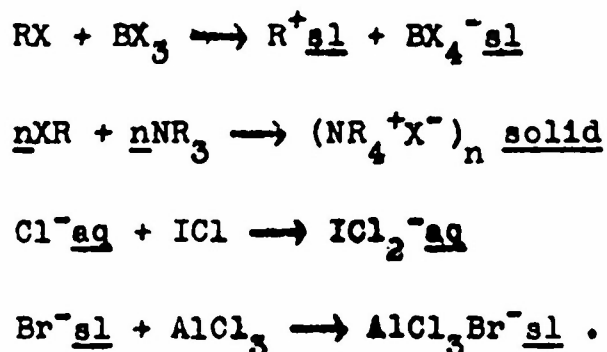
$$\psi(H_2^{+\cdot4}O^{-\cdot8},\ B^{+1\cdot8}F_3^{-\cdot6}) = \psi_0(H_2O,\ BF_3) \longrightarrow$$
$$\text{planar}$$
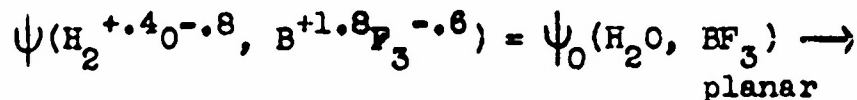
$$\left\{ \begin{array}{l} \underline{.2}\ \psi_0 \text{:}\ H_2O...BF_3 \\ \underline{.8}\ \psi_1 \text{:}\ H_2O^+_{\leftrightarrow}BF_3^- \end{array} \right\} = \tag{6}$$

$$\psi(H_2^{+\cdot6}O^{-\cdot4},\ B^{+1\cdot3}F_3^{-\cdot7}) = \psi\left[(H_2O)^{+\cdot8}(BF_3)^{-\cdot8}\right]$$
$$\text{pyramid}$$

The fact that $H_2O \cdot BF_3$ is an extremely powerful H-acid, $\underline{i.e.}$, $\underline{h}\sigma_d$ acceptor (yielding, with a base D, $DH^+\underline{es}$ + $(HOBF_3)^-\underline{es}$), is readily understandable if the charge distribution in the final product is somewhat as shown.

VIII. SYMMETRIZATION

Attention should be called briefly to a familiar phenomenon which is characteristic of the final stages of many donor-acceptor interactions. When for instance a donor of structure R_nZ interacts with a $\underline{k}\sigma_d$ acceptor of structure RQ to give $R_{n+1}Z^+$ + Q^-, the original donor and acceptor at first approach without special cognizance of the common possession of R atoms; but during the last stages of the reaction, more or less internal readjustment takes place in the R_nZ structure in such a way that all $\underline{n}$ + 1 R atoms become equivalent, with some extra gain in stability thereby. Processes of this kind and of the type $RQ + YQ_n \longrightarrow R^+ + YQ_{n+1}$ may be called $\underline{symmetrization}$ processes. Some typical examples ($\underline{sl}$ = solvent) are:

$$RX + BX_3 \longrightarrow R^+ \underline{sl} + BX_4^- \underline{sl}$$

$$\underline{n}XR + \underline{n}NR_3 \longrightarrow (NR_4^+X^-)_n \ \underline{solid}$$

$$Cl^- \underline{aq} + ICl \longrightarrow ICl_2^- \underline{aq}$$

$$Br^- \underline{sl} + AlCl_3 \longrightarrow AlCl_3Br^- \underline{sl} \ .$$

(7)

The last example is typical of the frequently occurring phenomenon of partial, or near-, symmetrization.

IX. INNER, OUTER, AND MIDDLE COMPLEXES

In a general consideration of the possible modes of interaction of a donor-acceptor pair, it is instructive to plot their energy of interaction $\underline{U}$ against a reaction coordinate $\underline{C}$. Without defining it precisely, let $\underline{C}$ be a quantity which increases continuously with charge transfer (that is, with $\underline{b}/\underline{a}$ in Eq. (1a), subject to the added specification that the nuclear skeleton be so adjusted for each value of $\underline{C}$ as to make $\underline{U}$ as small as possible. Thus $\underline{C}$ may be called a charge-transfer reaction coordinate, or simply a charge-transfer coordinate. A convenient scale for $\underline{C}$ runs from $\underline{C} = 0$ for $\underline{b}/\underline{a} = 0$ (donor and acceptor not yet in contact) to $\underline{C} = 1.0$ for some convenient state of maximum charge transfer. When (as is usual) $\underline{U}$ ($\underline{C}$) has a high maximum (activation energy), or an elevated minimum between two equal high maxima, this point may be taken as defining $\underline{C} = 0.5$.

As compared with the geometrically defined reaction coordinates used by Eyring, Polanyi, and others, the charge-transfer coordinate $\underline{C}$ is a little vague in that it is based on theoretical quantities which are not accurately known. Further, its exact relation to geometrical coordinates which change during a reaction is only roughly known; nor is it certain that in every case $\underline{C}$ at all times increases during the

actual path of a charge-transfer reaction. For the present purpose of a general survey, however, $\underline{C}$ is extremely convenient in that by its use the progress of a reaction can be completely specified in terms of a single coordinate, with possible exceptions as just noted.

As examples, reactions (5) and (6) may be considered. In (5), $\underline{C} = 0$ before the H_2O and HCl make contact, $\underline{C} = 0.5$ corresponds to some stage of the reaction where the H of HCl has moved part way toward the O of H_2O, and $\underline{C} = 1$ to the final stage of solvated $H_3O^+Cl^-$. At $\underline{C} = 0$, the H_2O and HCl are both neutral; at the intermediate stage ($\underline{C}$ probably near 0.5) indicated in (5), the summary charge distribution is $(H_2O)^{+.25}$ $(HCl)^{-.25}$; at $\underline{C} = 1$, the distribution is estimated as $(H_2O)^{+.5}(HCl)^{-.5}$. In (6), $\underline{C} = 0$ corresponds to neutral separate H_2O and BF_3, $\underline{C} = 1$ to an estimated $(H_2O)^{+.8}(BF_3)^{-.8}$.

Figures 1 and 2 contain several curves of $\underline{U}$ plotted against $\underline{C}$ for charge-transfer processes involving a donor D and an acceptor A, at least one of which is a closed-shell neutral molecule. The curves are schematic but illustrate probably the main types of behavior. Fig. 1 corresponds to interaction without benefit of solvent or other assist· ance. Fig. 2 is intended to illustrate the modifying effects of solvent assistance. In the curves of both Figures, the left hand minimum may be taken as defining $\underline{C} = 1$. For example, $\underline{C} = 1$ for NH_3 + HCl would correspond to ionic but undissociated $NH_4^+Cl^-$. The process of electrolytic dissociation, indicated in connection with curves II and III of Fig. 2 by auxiliary curves, is considered to proceed with $\underline{C}$ remaining essentially constant at the value 1.

The forms of the curves in Figs. 1 and 2 are based on a qualitative consideration of the expected energy behavior with increasing $\underline{C}$ of a varying succession of wave functions such as those illustrated by (5). Taking (5) as an example, it is convenient to start by placing

CAPTIONS FOR FIGURES

Figure 1. Energy curves $U(C)$ for unassisted interaction (inert solvent or none) between a donor D and an acceptor A. (Qualitative only; C = reaction coordinate, increasing from 0 toward 1 as b^2/a^2 in Eq. (3) increases.) The "outer complex" (C small), when present, corresponds to $b^2 \ll a^2$, the "inner complex" ($C = 1$) to $b^2 \approx a^2$ or $b^2 > a^2$.

Figure 2. Energy curves $U(C)$ for ionic-dissociative interaction between a donor D (e.g., NH_3) and a σ_d acceptor HX. (The curves would be similar for σ_d acceptors in general.) Curve I, unassisted. Curve II, same assisted by a weak and rather low-dielectric solvent (lower branch of curve is for dissociation of DH^+X^-S into solvated ions (S = solvent)). Curve III, like curve II but for strong and high-dielectric solvent. With the curves shown, little dissociation is expected with II, nearly 100% with III. (In the figure as printed, D should be substituted everywhere for B as the symbol for a donor molecule.)

Figure 3. Energy curves $U(C)$ for charge-transfer reactions of the type of Eqs. (8)-(9). "Middle complex" at $C = 0$ of curve III. $C = -1$, 0, and +1 here correspond more or less to $C = 0$, 0.5, and 1 of Figs. 1 and 2. In each curve, shallow depressions (outer complexes--cf. Figs. 1 and 2) near $C = \pm 1$ are an additional possibility.
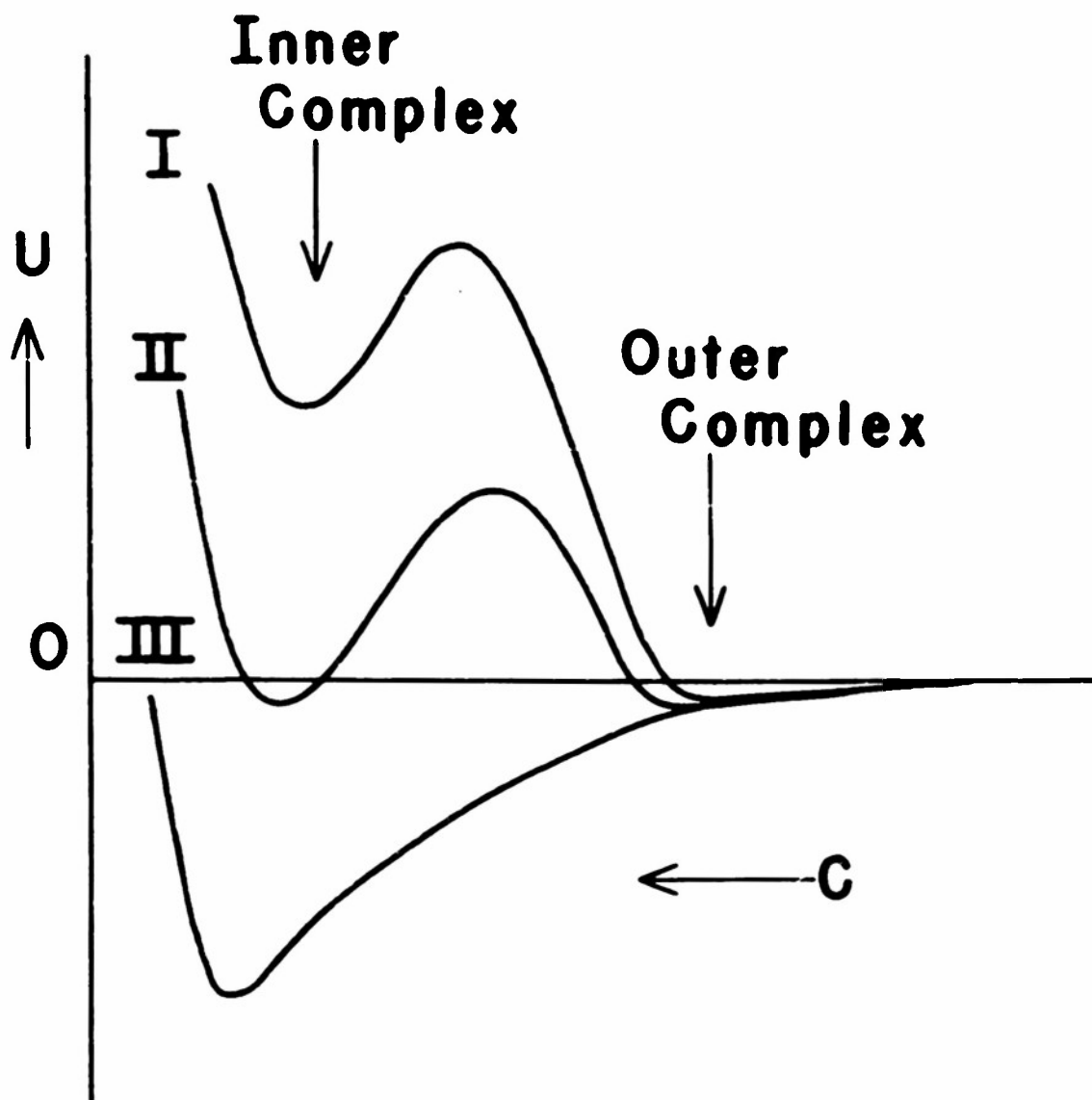
Eq. (1) describes the partial transfer of an electron from D to A; the ratio b^2/a^2, which is always between 0 and 1, measures the extent of transfer. It does not necessarily demand either (1) sharing of an electron pair, or (2) that the transferred electron shall come strictly from one particular atom in D and go strictly to one particular atom in A. However, it does not exclude these as important special cases. Lewis's and Sidgwick's use of restrictions (1) and (2) in setting up their formal definitions (cf. acids and bases, or acceptors and donors), though seeming natural at the time, has had some tendency to inhibit others from making the fullest or freest use of the inherent possibilities of the donor-acceptor concept. Also, without an explicit quantum-mechanical formulation, the nature of partial electron transfer has tended to appear rather obscure; in particular, the validity of the donor-acceptor interaction concept for explaining the many loose organic molecular complexes has not always been seen in a clear light.[2]

Ingold's definitions dropped the first of the two limitations in Lewis's, but did not clearly dispose of the second. The present definition, as given above in words and in quantum-mechanical form, definitely drops both. In dropping the second limitation, it permits one, in general, to think in terms of intermolecular donor-acceptor action between molecules as wholes--an idea which may be considered as a generalization of that used by Dewar in his concept of π-complexes.

The simple quantum-mechanical viewpoint expressed in Eq. (1) makes clearer the justifiability of the inclusion by Ingold and others of bases and reducing agents in a single class (donors) and of Lewis acids and oxidizing agents in another (acceptors). It goes further in showing that there is perhaps even no fundamental need in terms of theory to distinguish bases and reducing agents as subclasses of the class "acceptor". These distinctions now appear as perhaps matters of
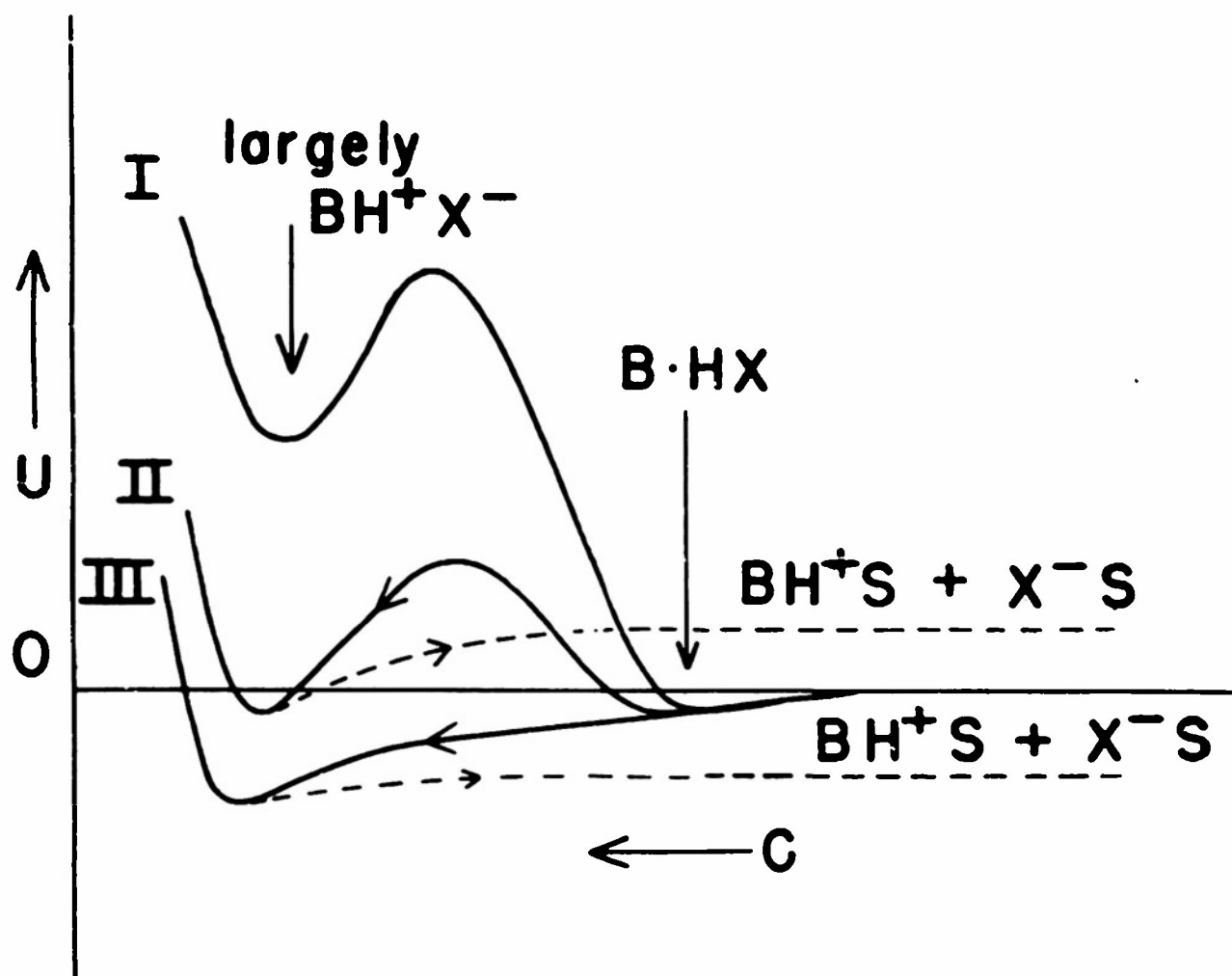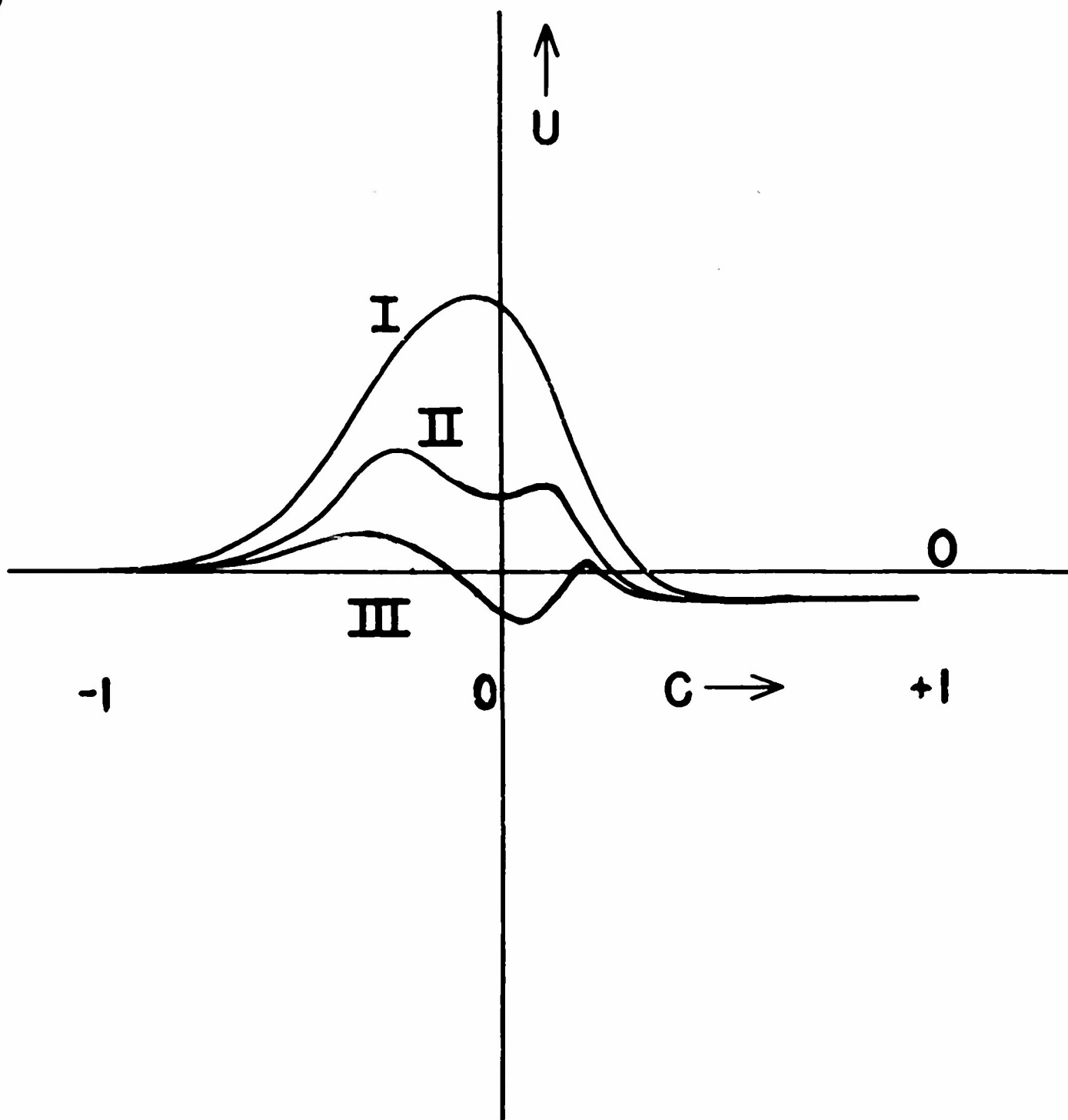
the HCl near the H_2O with the H directly between the Cl and the O, and with the Cl at a distance from the O equal to that in the (ionic but un-dissociated) reaction product $H_3O^+Cl^-$. For this state of affairs, $\underline{C}$ would still be only a little larger than zero. If now $\underline{C}$ is allowed to increase, the H atom moves toward the O atom. The O—Cl distance, though regulated only by the specification that it so adjust itself as to keep $\underline{U}$ as low as possible for any value of $\underline{C}$, very likely remains nearly constant. As $\underline{C}$ increases, $\underline{U}$ tends to increase because (1) the nonbonded repulsions within ψ_0 (see (5)) increase; and (2) the amount $(\underline{b}^2/\underline{a}^2)$ of the higher-energy wave function ψ_1 increases. On the other hand, the following factors work increasingly to diminish $\underline{U}$ as $\underline{C}$ increases: (1) electrostatic polarization within ψ_0 (increase of the $H_2O...H^+...Cl^-$ resonance component); (2) decrease in the energy of ψ_1, because of increasing attractions and decreasing repulsions as the H moves toward the O atom; (3) decrease in the energy of ψ_1, because of "dative polarization" (readjustment of the relative proportions of the resonance components--probably increase of $H_2O^+ \text{---} H \longleftrightarrow Cl^-$ relative to $H_2O^+...H \longleftrightarrow Cl$, the latter being probably at maximum importance near $\underline{C} = 0$),[20] within ψ_1; (4) resonance between ψ_1 and ψ_0.[21] Figs. 1 and 2

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[21] In complex-formation in general, valence bond rearrangements such as can occur without charge-transfer (as, $\underline{e}.\underline{g}.$, in $H_2 + I_2 \longrightarrow 2HI$) should also contribute to cutting down $\underline{U}$ by resonance.

---

differ in that the electrostatic forces of the solvent progressively lower $\underline{U}$ $(\underline{C})$, as $\underline{C}$ increases, in Fig. 2 as compared with Fig. 1.

The net outcome of the factors just outlined should be curves like those in Figs. 1 and 2, the typical case being one with an "outer complex" ($\underline{C}$ small) and an "inner complex" ($\underline{C} = 1$), with a maximum ($\underline{C} = 0.5$) between. These maxima, or barriers, may be identified with

"activated complexes" of chemical kinetics. The inner complexes when not inaccessibly high, yet not stable enough to be end-products, may often be identifiable with "reaction intermediates".

In Fig. 1, additional variations would include curves with no inner minimum. Another possibility is a curve like I, but with a small barrier outside the outer minimum. An example is the loose $I_2 \cdot Pr$ complex (Pr = propylene), concerning which it is reported[22] that iodine in

[22] S. Freed and K. M. Sancier, J. Am. Chem. Soc., 74, 1273 (1952).

solution at 77° K. in propane, an inert solvent, upon addition of Pr, develops the color of the $I_2 \cdot Pr$ complex only slowly, indicating a small outer barrier.

It seems probable that among n-donor, v-acceptor pairs, reacting without solvent assistance, examples of reaction curves of all the types I, II, and III of Fig. 1, and/or variations of these, occur. For a case like BCl_3 + NMe_3, type III seems probable;[23] type I might be ob-

[23] This is supported by recent work of D. Garvin and G. B. Kistiakowsky, J. Chem. Phys., 20, 105 (1952).

tained for BR_3 + NR_3, using bulky R and R' groups[24] to cause steric hin-

[24] See especially the papers of H. C. Brown and collaborators, mainly in J. Am. Chem. Soc.

drance.

The preceding discussion needs amendment in one respect, namely, that besides charge-transfer forces, additional attractive forces--associated with the ψ_0 component of the wave function--may participate in creating loose complexes. For every pair of neutral entities (A,B), London dispersion forces give of course at least a weak van der

Waals attraction. In addition, classical electrostatic forces must tend to give loose complexes whenever A and/or B is an ion or has a dipole moment. The so-called hydrogen bond[25] falls in this category.
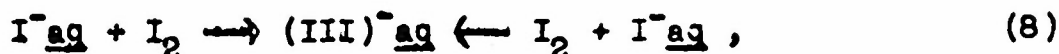
[25] See L. Pauling, The Nature of the Chemical Bond (Cornell University Press), Chapter IX.

It is generally believed that hydrogen bonding is usually primarily electrostatic, but often with some additional stabilization by donor-acceptor forces. In the extreme case of HF_2^- formed from $HF + F^-$, assisted symmetrized charge-transfer binding apparently predominates over pure electrostatic binding. In a similar way, charge-transfer binding apparently predominates over electrostatic polarization-binding in the formation of I_3^- from $I_2 + I^-$.[26]

[26] Cf. G. C. Pimentel, J. Chem. Phys., 19, 446 (1951), for a discussion (using nonlocalized-MO methods) of the linear ions (FHF)⁻ and I_3^- essentially as symmetrized charge-transfer complexes. (In I_3^-, partial trivalency of the central I atom probably also assists.)

In many cases, it is difficult to set up experimental criteria to establish whether the stability of a given loose complex is due more to purely classical electrostatic attraction or more or less to charge-transfer resonance, and theoretical considerations must be used. Some interesting examples of probably purely electrostatic H-bonded complexes which simulate donor-acceptor complexes are discussed in Table IV (see types $b\pi + h\sigma$ and $b\pi + k\sigma$, Part 19 of table).

Instead of Figs. 1 and 2, another kind of diagram, in which values of the reaction coordinate $\underline{C}$ ranging from -1 to +1 are assigned, is useful for certain charge-transfer reactions; in particular those involving $\underline{n}'$ donors and $\underline{x}\sigma$ or $\underline{h}\sigma$ acceptors, for example:

$$I^-aq + I_2 \longrightarrow (III)^-aq \longleftarrow I_2 + I^-aq , \qquad (8)$$

and

$$HO^-aq + MeI \longrightarrow (HOMeI)^-aq \longrightarrow HOMe + I^-aq . \qquad (9)$$
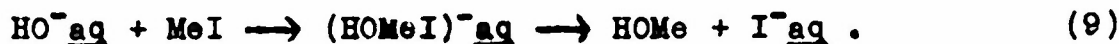
Fig. 3 shows typical curves for reactions like these. Curves I and II correspond to the case where the reaction proceeds continuously to the right over an activation barrier or barriers, as in the typical displacement reaction (9). The stable complex occurring near $C = 0$ in cases like curve III may be referred to as a "middle complex". This corresponds to the "activated complex" of Cases I and II and of Figs. 1 and 2. Reaction (8) corresponds to a special case of curve III of Fig. 3 with equal values of U for large positive and negative values of C.[26]

The relevance of Fig. 1 to the interactions of n donors with v acceptors has been discussed above. Figs. 1 and 2 are further especially applicable to the interactions of n and π donors with σ acceptors. In the absence of solvent or other assistance, these usually form loose dative complexes (or, for $h\sigma$ and $k\sigma$ acceptors, probably only H-bonded complexes or none at all--see discussion under reaction-type 14 in Table IV). These are "outer" complexes, but it seems probable that more-or-less-pure-ionic "inner" complexes exist in all such cases (including those with $h\sigma$ and $k\sigma$ acceptors) as activated states, corresponding to $U(C)$ curves like curve I in Fig. 1 (the outer minimum should be omitted for $h\sigma$ and $k\sigma$ acceptors). It may be, however, that in special cases, the energy of the inner complex is nearly as low (cf. curve II of Fig. 1) as that of the outer complex, or even slightly lower, so that both forms may exist in equilibrium (see discussion under reaction-type 14 in Table IV for some possible examples).

It will be noted that inner and outer complexes here corres-
pond respectively (with respect to at least one of the two partners) to
what have been called associative and dissociative functioning (sub-
scripts a and d) in Section II and the Tables--dissociative in the
sense that a covalent bond originally present is broken or nearly broken
in the inner complex, even though in the absence of an ionizing solvent
the parts still cohere because of ionic attraction (and some residual
covalence).

With es or auxiliary-acceptor assistance ("conditional" func-
tioning of the donor-acceptor pair--see Section VI), the curves of Fig.
1 are modified, the energy of the inner complex always being lowered,
so that if the assistance is strong enough, the inner complex becomes
the stable form of the donor-acceptor pair (cf. curves II and III in
Fig. 2). In addition, more or less complete separation into independ-
ent solvated ions may occur as a secondary process (dashed curves in
Fig. 2) if the assisting agent is sufficiently an ionizing solvent. In
this typical situation, the term "dissociative" becomes especially ap-
propriate. If the assisting agent is ionic-crystal formation, a sort of
polymerization rather than a separation of the ions occurs; however, the
action is still dissociative in the sense mentioned in the preceding
paragraph.

The behavior of σ donors (structure RQ) with v acceptors is
probably closely analogous to that of n donors with $k\sigma$ acceptors (struc-
ture RQ). Namely, probably no stable outer complex is formed, and prob-
ably without assistance the inner complex is an activated state; but
with sufficiently strong solvent or ionic-crystallization assistance the
inner complex becomes the ground state.

Thus for many types of donor-acceptor pair, the existence of
two modes of interaction corresponding to the inner and outer complexes

of Figs. 1 and 2, separated by an activation barrier, with the one or
the other mode the more stable depending on environment, is probably
typical. For the outer complex, when this exists, the interaction is
always associative. For the inner complex, it is associative with re-
spect to the donor and dissociative with respect to the acceptor in the
case of σ acceptors and $\underline{n}$ donors. For σ acceptors with π donors, the
functioning of the latter, though classed as dissociative ($\underline{b}\pi_d$) because
a π bond is broken internally, is in a more obvious sense associative
(cf. Table III). In the case of σ donors with $\underline{v}$ acceptors, the roles
of the former and latter are respectively analogous, with regard to as-
sociative or dissociative behavior, to those of σ acceptors with $\underline{n}$ don-
ors.

For the interactions of $\underline{n}'$ donors (or $\underline{v}^*$ acceptors), a $\underline{U}(\underline{C})$
diagram more or less of the type of those in Fig. 3 is applicable. The
mid-point in Fig. 3 corresponds to the activation barrier in Figs. 1-2,
but the end-points in Fig. 3 are symmetrically related as to charge dis-
tribution, contrasting with Figs. 1-2 where the outer and inner com-
plexes are very unsymmetrically related (the one involving essentially
neutral molecules, the other being more or less completely ionic). In
many reactions, the mid-point in Fig. 3 corresponds to an activated
state, but in some ($\underline{n} + \underline{v}^*$, $\underline{n}' + \underline{v}$, $\underline{n}' + \underline{x}\sigma_a$, and the rare cases of $\underline{n}'$
$+ \underline{h}\sigma_a$) to a stable minimum; it seems likely that similar cases of the
type $\underline{b}\sigma_a + \underline{v}^*$ also occur.

<div align="center">*   *   *</div>

The charge-transfer-process idea, with the aid of Figs. 1-3,
appears capable of giving plausible indications about reaction-paths for
a great variety of chemical reactions. However, great caution will be
needed in attempting to apply the idea to the determination of what ac-
tually happens in specific reactions, since the possible paths, even

for a single over-all reaction, are often numerous, diverse in type, and complicated, and dependent on the nature of the medium and on other factors.

X. CORRECTIONS AND IMPROVEMENTS ON PREVIOUS PAPERS

Some improvements in the donor and acceptor classes and classification symbols of Paper II[2] are described in Section II above. An error in quoting spectroscopic data on $Et_2O \cdot I_2$ in Paper I[4] is corrected in Table IV (reaction-type 13, footnote $\underline{v}$). A revision of Fig. 5 of Paper II is described in Table IV (reaction-type 7, footnote $\underline{m}$). An overlooked reference of some importance relevant to Paper I is: Childs and Wolker, Trans. Faraday Soc., 34, 1506 (1938), on the spectra of bromine in benzene, acetic acid, water, and ethyl alcohol.

In Paper I, on page 606, the two pairs of resonance structures given for $R'RO \cdot I_2$, and called (I) and (II), are not independent; pair (II) should be dropped. Resonance between the two equivalent forms (I) gives I_2^- 3-electron bonding $\underline{together}$ with $O^{\pm}$—I electron-pair bonding, the two effects being nearly but not quite additive so long as the O^+—I bonding is weak.

ACKNOWLEDGEMENT

practical convenience rather than of basic theory. However, the ques-
tion of course deserves much more thorough consideration than the brief
and preliminary comments made here. An important point to be kept in
mind in such a more thorough study is perhaps the fact that the terms
"oxidization" and "reduction" are generally used for over-all processes,
and often in more or less formalistic ways with respect to assignments
of charges to atoms; whereas very often (not always) the concepts of
Lewis acids and bases (or electrophilic and nucleophilic reagents) are
used in connection with (real or supposed) actual mechanisms of reac-
tions.

In terms of Lewis's definition calling for the sharing of an
electron pair, acceptors such as BF_3 and H^+ (if it existed free) were
clear cases of typical acids. Oddly enough, Lewis appears to have
found it a little awkward to include the H-acids, for example HCl, as
acids at all per se (that is, in the absence of ionizing solvents)--as
can be inferred from Lewis's 1938 paper,[5] and from Luder and Zuffanti's
book.[6]

Luder and Zuffanti describe H-acids HQ as secondary acids, in
the sense that, while they are not really Lewis acids themselves, they
are capable of supplying a Lewis acid (namely H^+) to a base. [That is,
they are proton donors, or Lewis-acid donors.] These secondary Lewis
acids are thus thought of as composites of a primary Lewis acid (H^+)
and a base (Q^-); and in a similar way other conceivable composites of
primary Lewis acids and bases can be described as secondary Lewis acids.
[The same or similar composites could equally be described as secondary
bases.] For example, various covalent compounds RQ, likewise such typi-
cal compounds of primary Lewis acids and bases as $H_3N \longrightarrow BMe_3$, may be
considered as secondary Lewis acids [or as secondary bases]. (See also
Table IV, footnote d.) The matter of the classification of H-acids and

various other molecules RQ as acceptors will be discussed rather thoroughly below.

Meanwhile, it may be noted that Ingold had no hesitation in classifying molecules such as HQ and RQ as electrophilic reagents. (From a similar point of view, Usanovich classified HQ and RQ as acids.[10]) In so doing, Ingold pointed out briefly (Ref. 9, p. 269) that electrophilic reagents can be subdivided into classes in various ways, one such subdivision being into two types which may be called associative acceptors (e.g., BF_3) and dissociative acceptors (e.g., HQ or RQ).

In a preceding paper,[2] a classification of donors and acceptors into a number of distinct types was outlined. This has been somewhat revised, extended, and clarified in Tables I-IV below. Using this classification, the present formulation (like Ingold's) seems among other things to make it easier to treat under a unified scheme and viewpoint the action of one and the same donor molecule in such different activities as are expressed by, for instance:

$$H_2O + BF_3 \longrightarrow H_2O{\rightarrow}BF_3 \qquad (2)$$

and

$$H_2O + HCl \xrightarrow{aq} H_3O^+aq + Cl^-aq . \qquad (3)$$
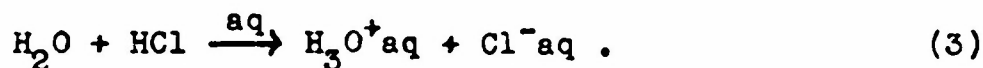
The first action (with a good L-acid) is purely associative, the second (with a good H-acid) is an ionogenic displacement reaction; from the viewpoint of the H-acid acceptor, it is dissociative. What the two reactions have in common is (1) partial transfer of an electron from the donor H_2O to the acceptor, and (2) formation of a (somewhat incomplete, or partial) dative bond between the donor and the acceptor. In the second reaction, of course, an additional thing happens: namely, splitting of the acceptor into an ion Cl^- and a (partially positive) H atom,

it being the latter, rather than the acceptor as a whole, which unites covalently with the (strongly positively charged) H_2O to form the dative bond.[11]

> [11] How best to describe what happens in reactions like (2) has of course long been a moot question. See for example Ref. 7, pp. 68, 114, on the similar case of NH_3 + HCl.

While the commonly used description of the second reaction as a proton transfer reaction is very convenient, it is open to two criticisms: (1) it is only formal or schematic, in the sense that at no time during the process of transfer is the proton really more than partially free from an electron (in other words, the proton carries a large fraction of an electron with it during its transfer); (2) it ignores the important fact of concurrent partial electron transfer from the H_2O. If (2) is ignored, the fruitful possibility of a unified common classification of the two reactions as electron donor-acceptor reactions is thrown away. A more detailed analysis of reaction (3) is given in Section VII.

Here it may further be noted that Luder and Zuffanti in describing H-acids as secondary Lewis acids have adopted the same proton-transfer viewpoint as was used by Brønsted and Lowry. In the present viewpoint (as also apparently in Ingold's concept of electrophilic reagents), the H-acids HQ, together with other molecules RQ, are classified directly as acceptors in their own right along with primary Lewis acids, such as BF_3. According to this viewpoint, while it is true that an acceptor like HCl can be regarded formally as a compound of another acceptor H^+ and a donor Cl^-, _physically_ according to quantum mechanics the structure is believed to be much more nearly covalent than ionic.